Long-Term Thermo-Oxidative Degradation of High-Temperature Polymers and their Composites

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Workshop #3: Exploring the Pivotal Role of Next Generation X-rays in Bridging the Scale-Gaps in Next Generation Energy Materials under Extremes
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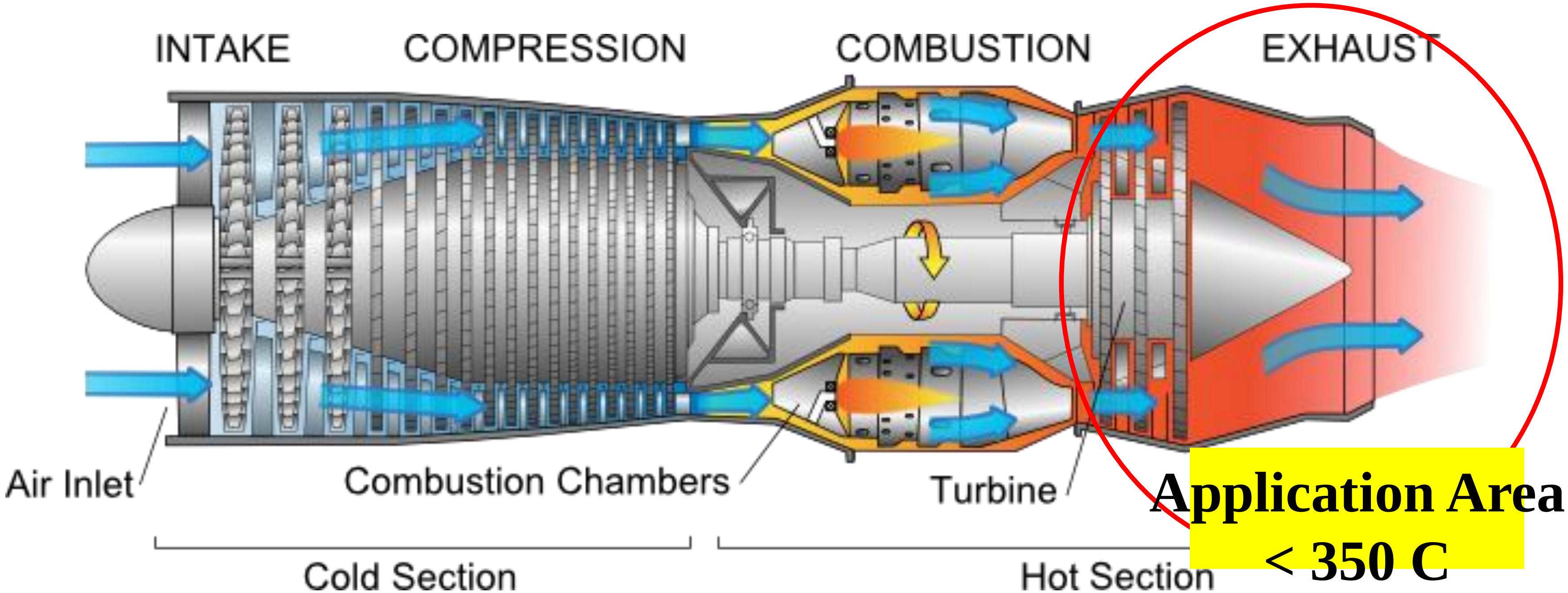
May 19th, 2014

High Temperature Composites & Aging



Age-Related Degradation

1. Physical aging, including the creep and relaxation of the matrix and fiber-matrix interphase;

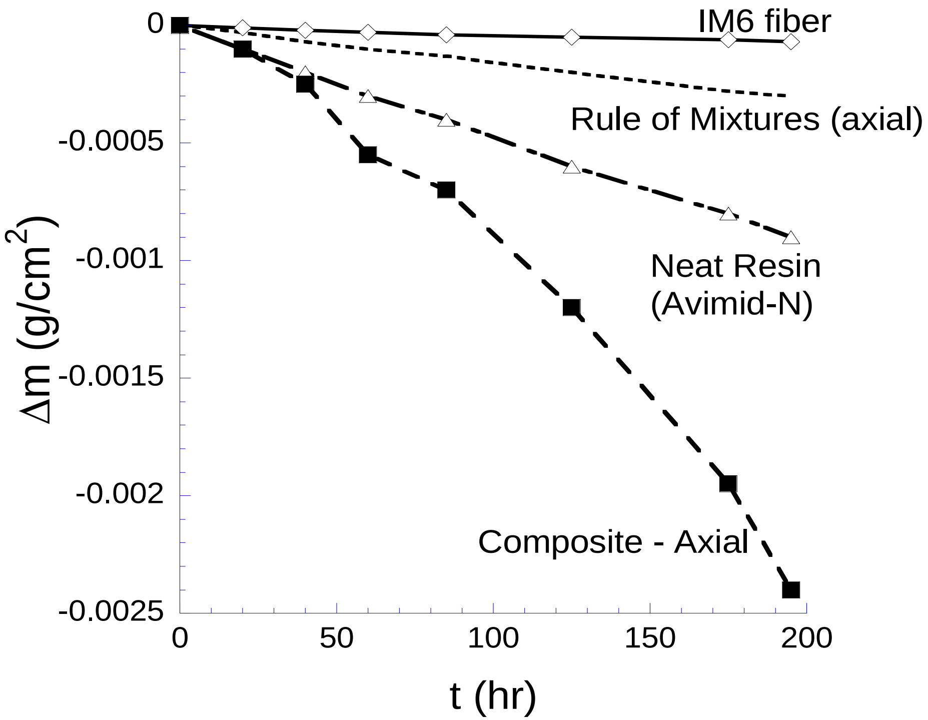
2. Chemical aging, controlled by the thermo-oxidative degradation of the matrix and fiber-matrix interphase;

3. Micromechanical damage growth and failure

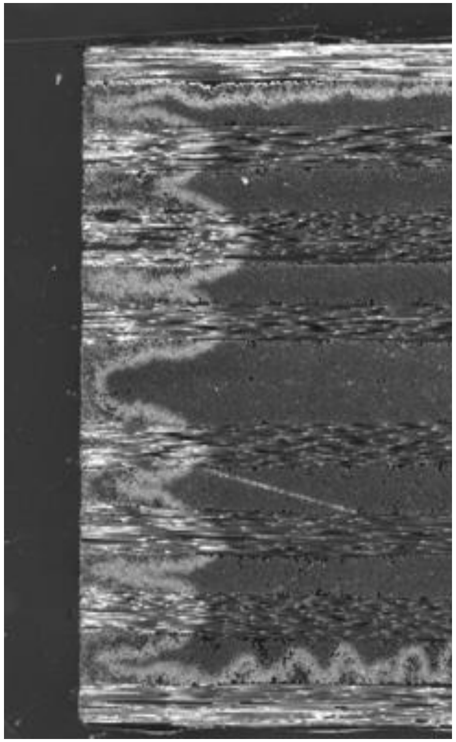
Oxidation of Polymers and Composites

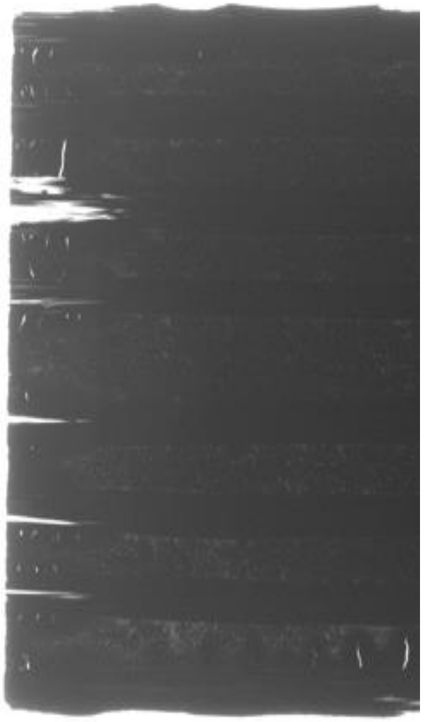
Avimid-N/IM6 (650°F/343°C)

Wang, Chen, Skontorp,2003



Weight Loss?



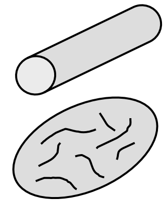


Tandon et al. 2011

TOS is orthotropic and heterogeneous in Lamina
Weight loss of constituents cannot be used for composite design

Goal: A Scalable Methodology

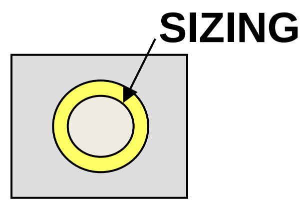
Fiber and Matrix



- Degradation mechanisms
- Thermal-oxidative characterization
- Hygrothermal degradation

Constituent Properties

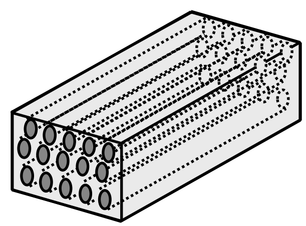
Unit Cell



- Interface/interphase TOS degradation characterization
- Orthotropic TOS response

Lamina Parameters

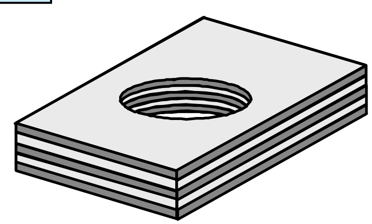
Lamina



- D_{ij}^{c} effective diffusivity
- E'_{ij}, E''_{ij} effective moduli
- Effective damage (spatial/temporal variation)

Layup/Stacking Sequence

Laminate Response



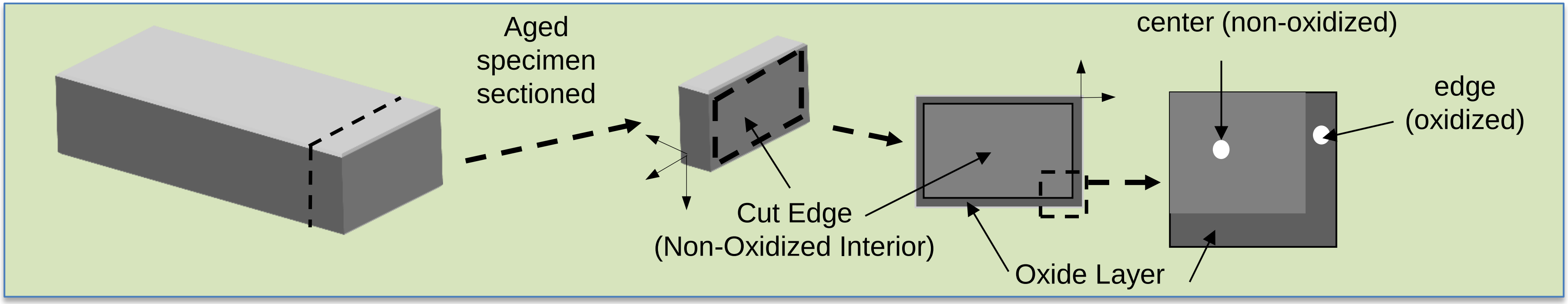
- Diffusion/Sorption growth
- Laminate response prediction

  $\sigma(x,y,z,t)$

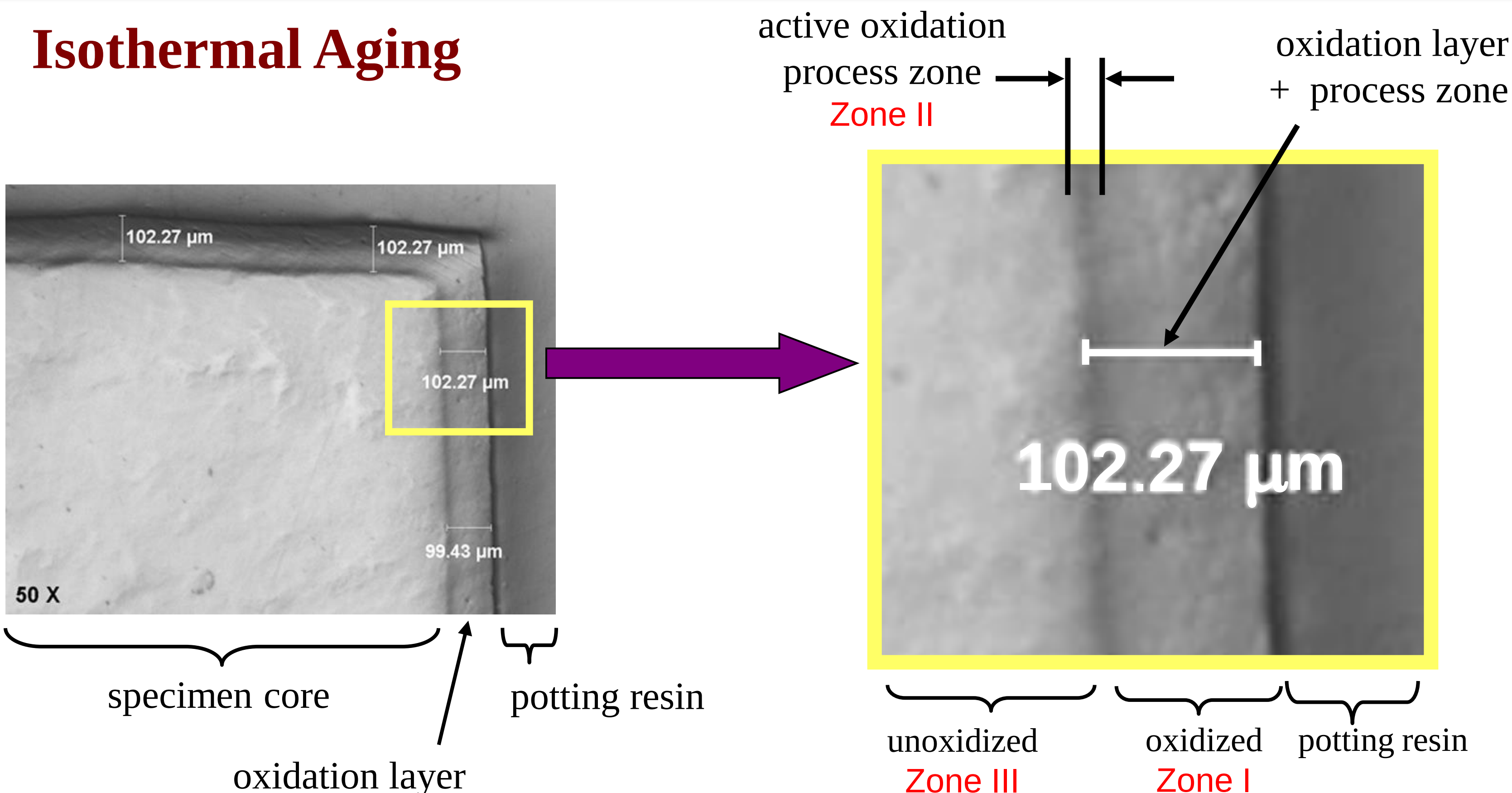
  $\varepsilon(x,y,z,t)$

Isothermal Aging Studies

Oxidation Layer Size and Growth

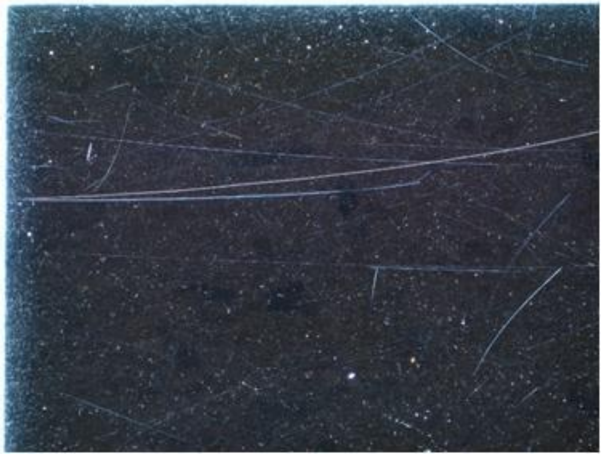


Isothermal Aging



Optical Microscopy

Bright-Field



Dark-field

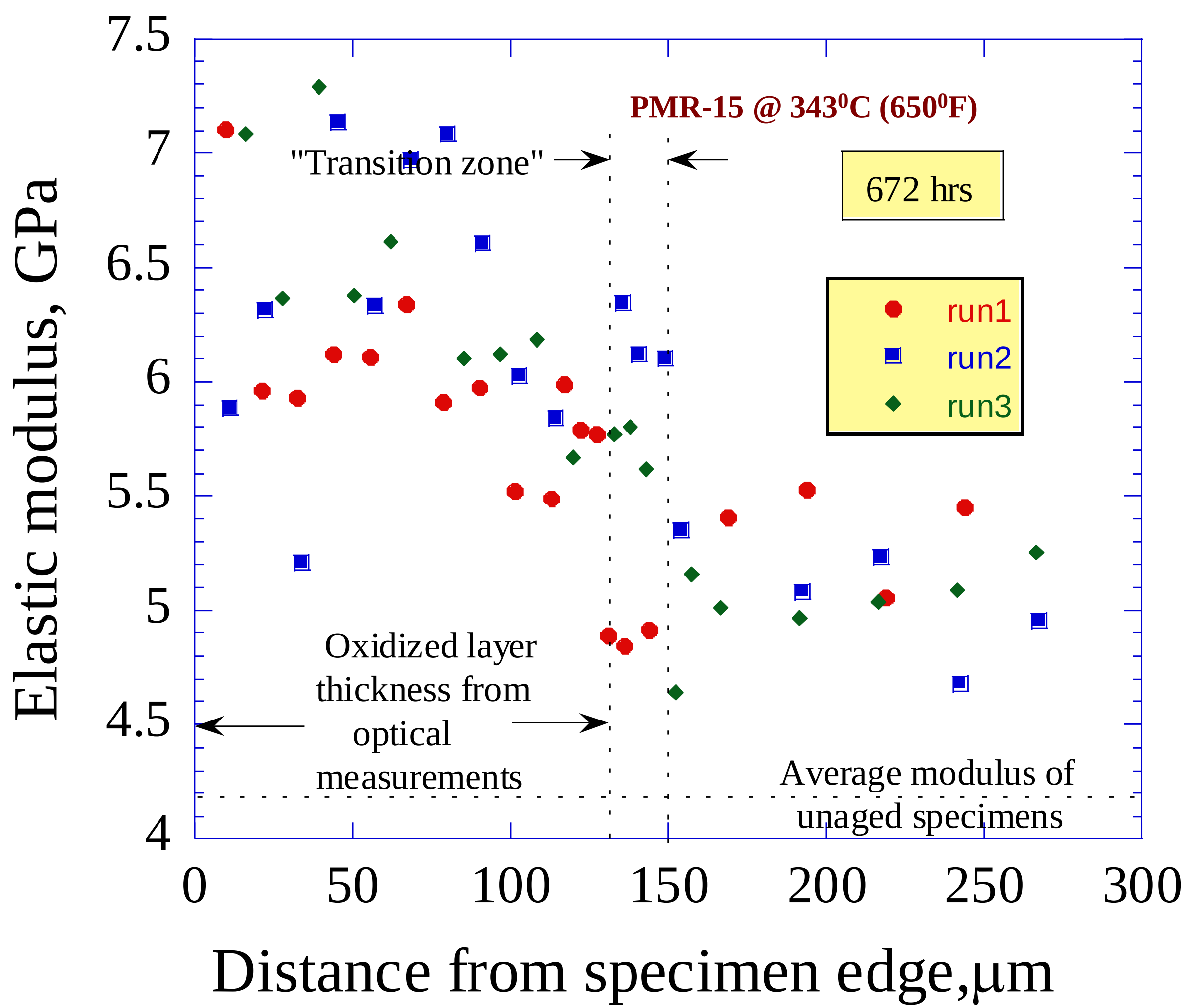
Fluorescence

Differential Interference Contrast

- Previously used techniques (*bright-field, dark-field, fluorescence imaging*) unable to track oxidation growth in neat resin
- A new technique based on differences in index of refraction of oxidized and unoxidized regions is successful

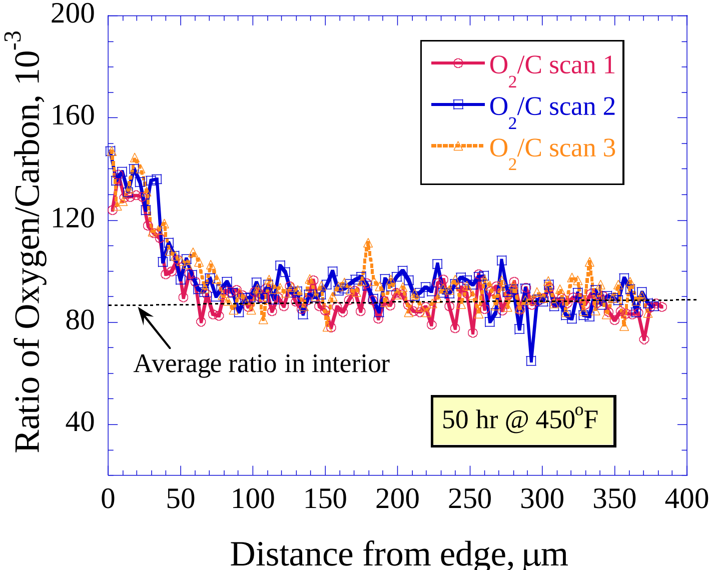
Tandon, et al 2011

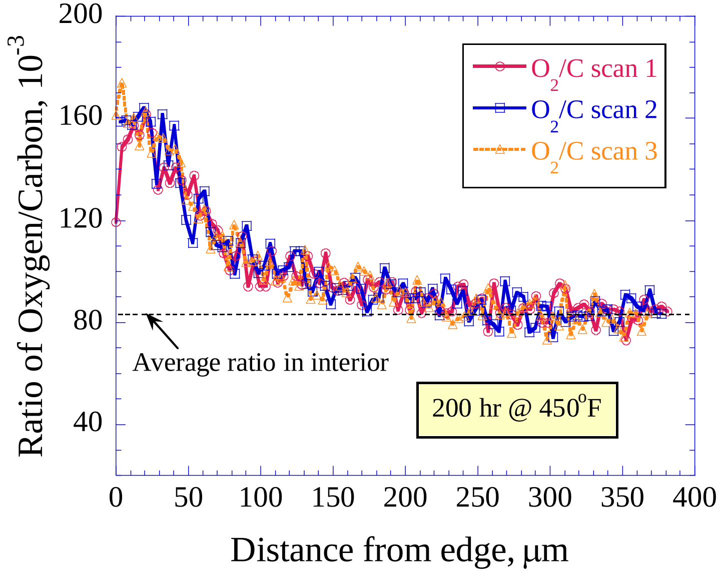
Oxidation Layer Characterization: Nano-indentation

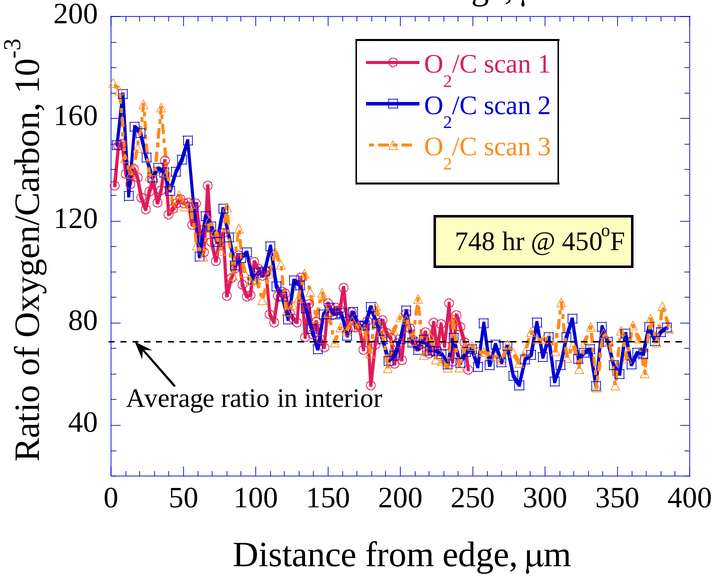


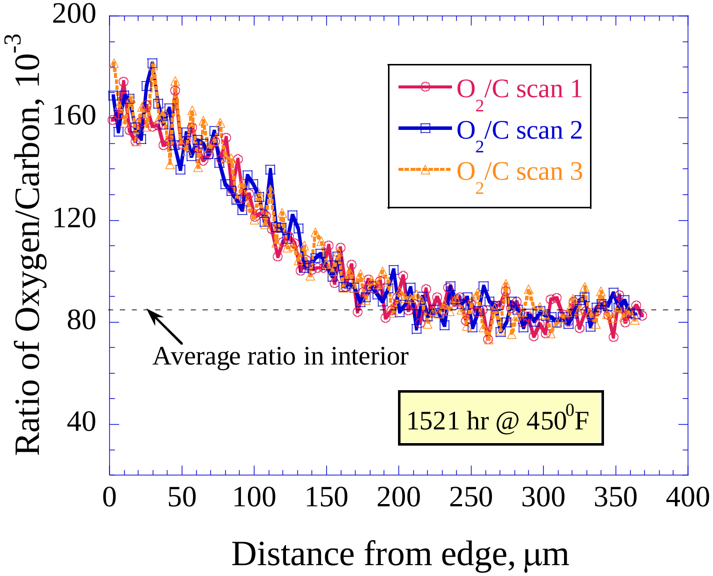
- Oxidation transition zone between oxidized edge zone and specimen interior remains relatively constant for all aging times.
- Significant increases in resin stiffness in oxidation layer.

Energy Dispersive Spectroscopy



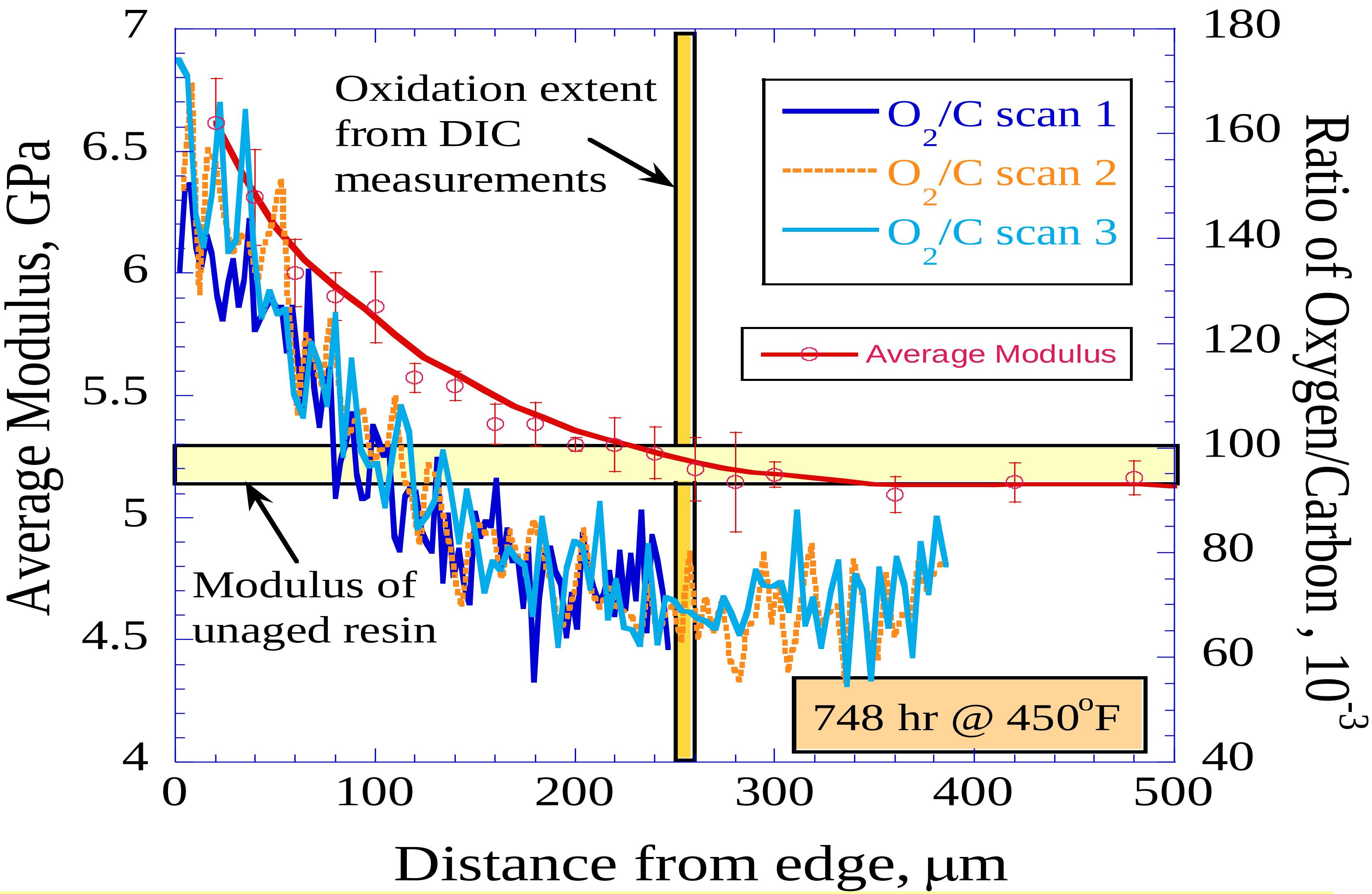






- Chemical depth profiling using the Genesis elemental analysis software
- Relative oxygen content is higher in the oxidized region
- Distribution provides estimation of the extent of the oxidized region

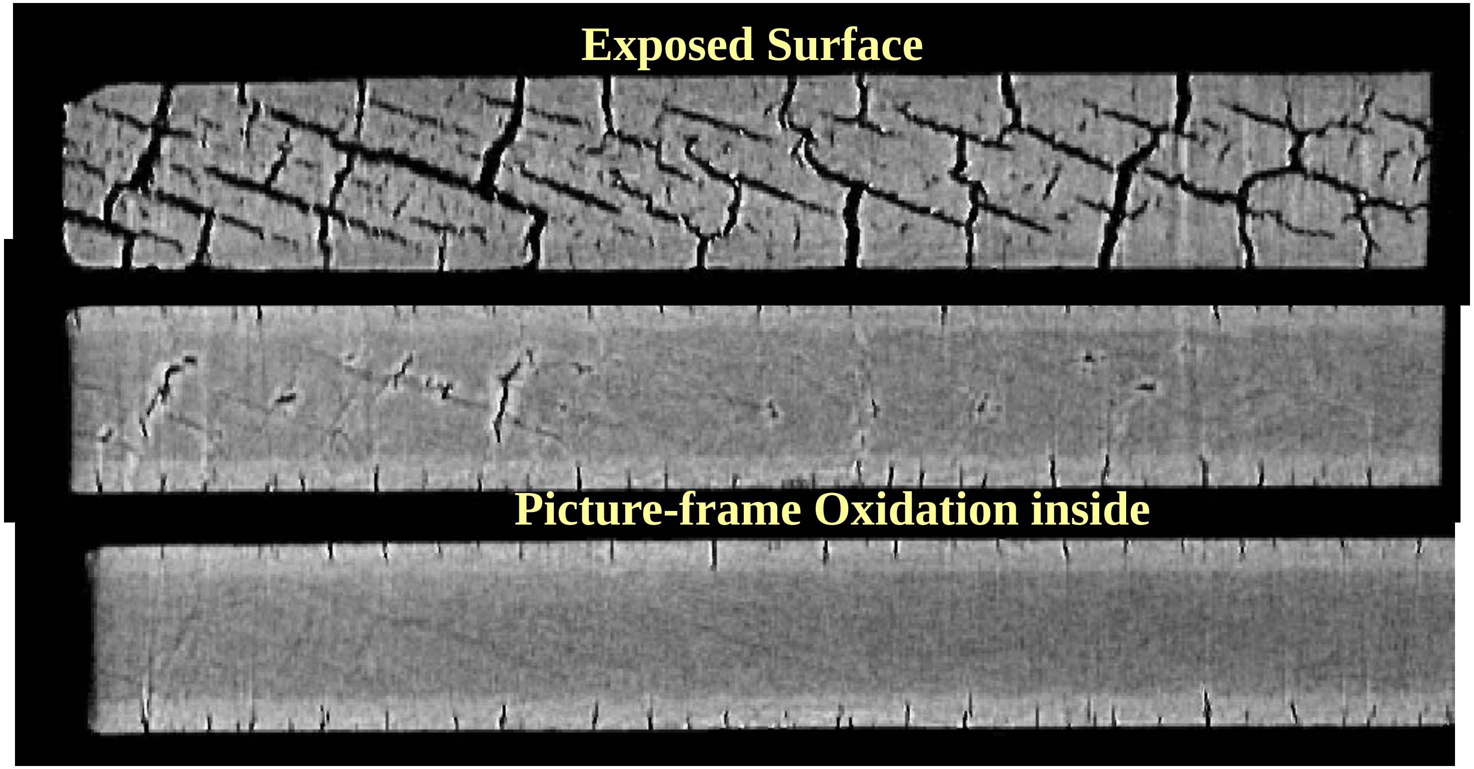
Comparison of Mechanical, Optical and Chemical Mapping



Different techniques validate extent of oxidized region

Oxidation Layer Characterization: CT Scanning

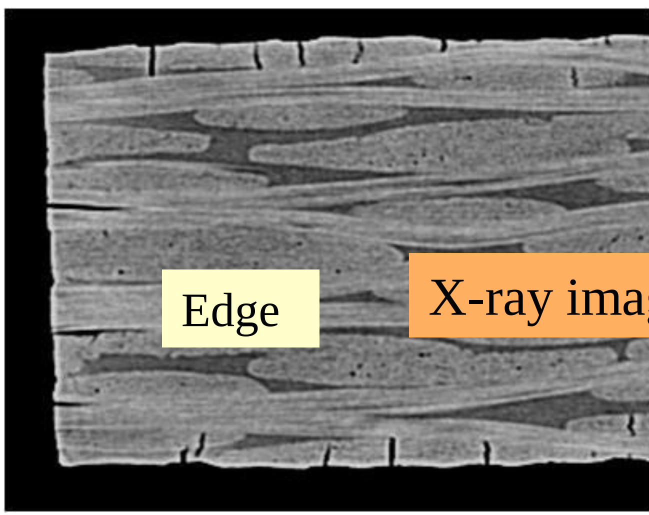
PMR-15 aged for 3112 hrs

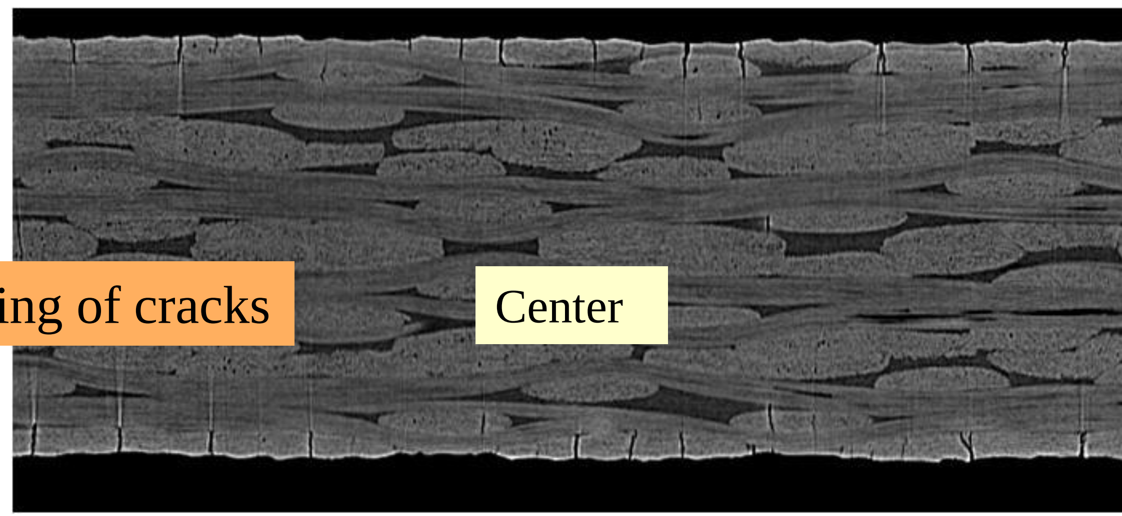


- CT scans show the damage and oxidation layer sides in the specimen
- Oxidation layer thickness can be correlated to those obtained from other techniques
- Crack length and density can be determined throughout the entire specimen

Validation of Optical Microscopy Technique for Damage Assessment

3000 hr
@ 450ºF

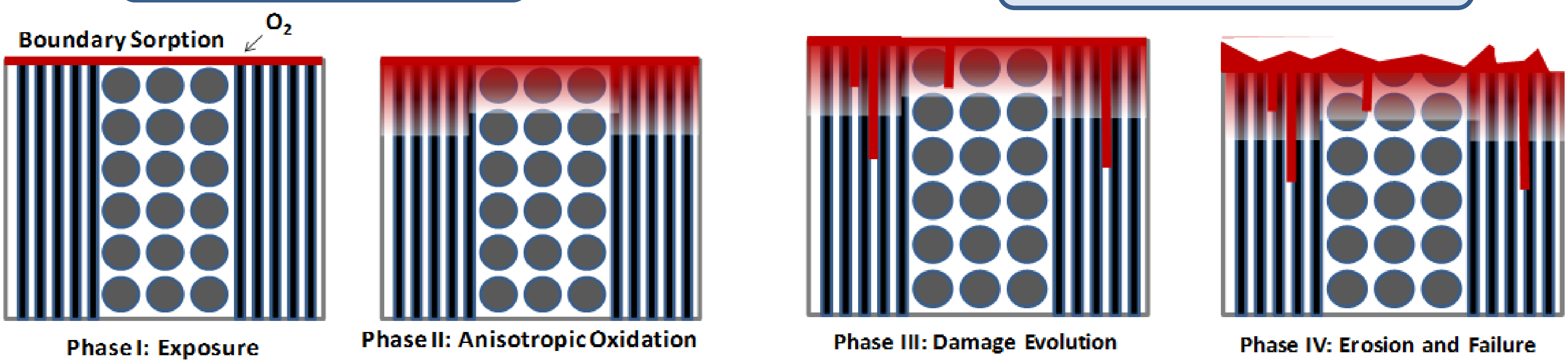




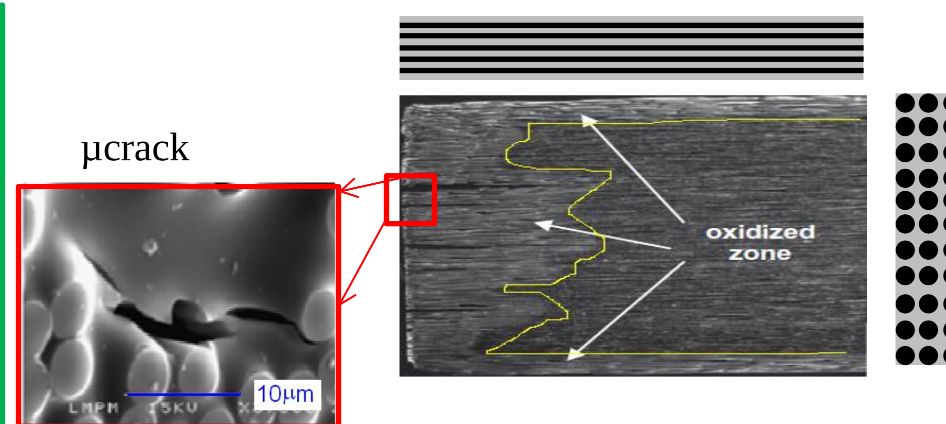
- Polished discrete section is representative of the damage behavior in the interior
- Similar damage growth and distribution observed

Mechanisms of Oxidative Degradation

Oxidation → Oxidative Degradation

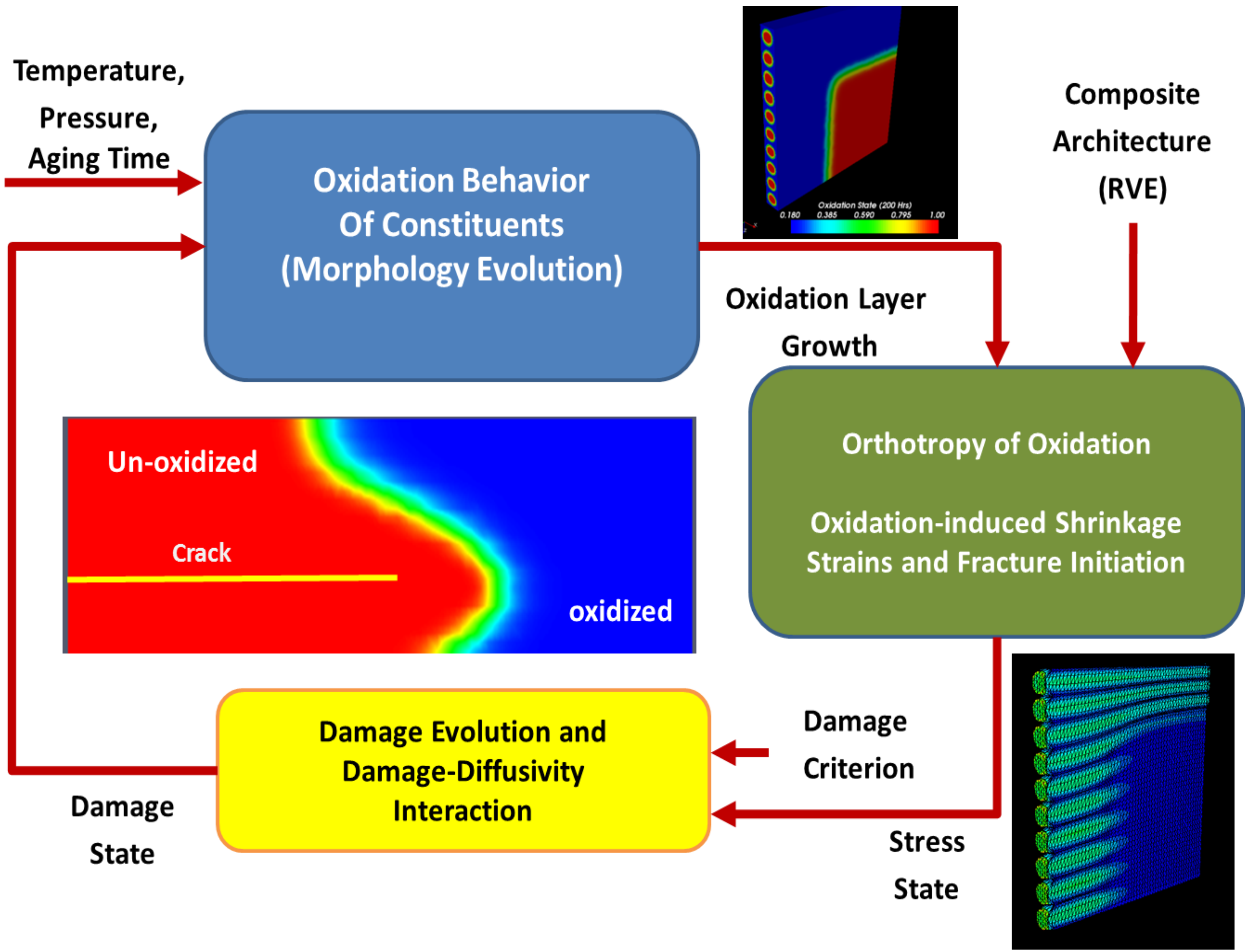


- Phase I: Exposure and boundary sorption
- Phase II: Heterogeneity in diffusivity induces anisotropic oxidation
- Phase III: Conversion into oxide products induces oxidation-driven strain and damage evolution
- Phase IV: Newly formed surfaces promotes diffusion

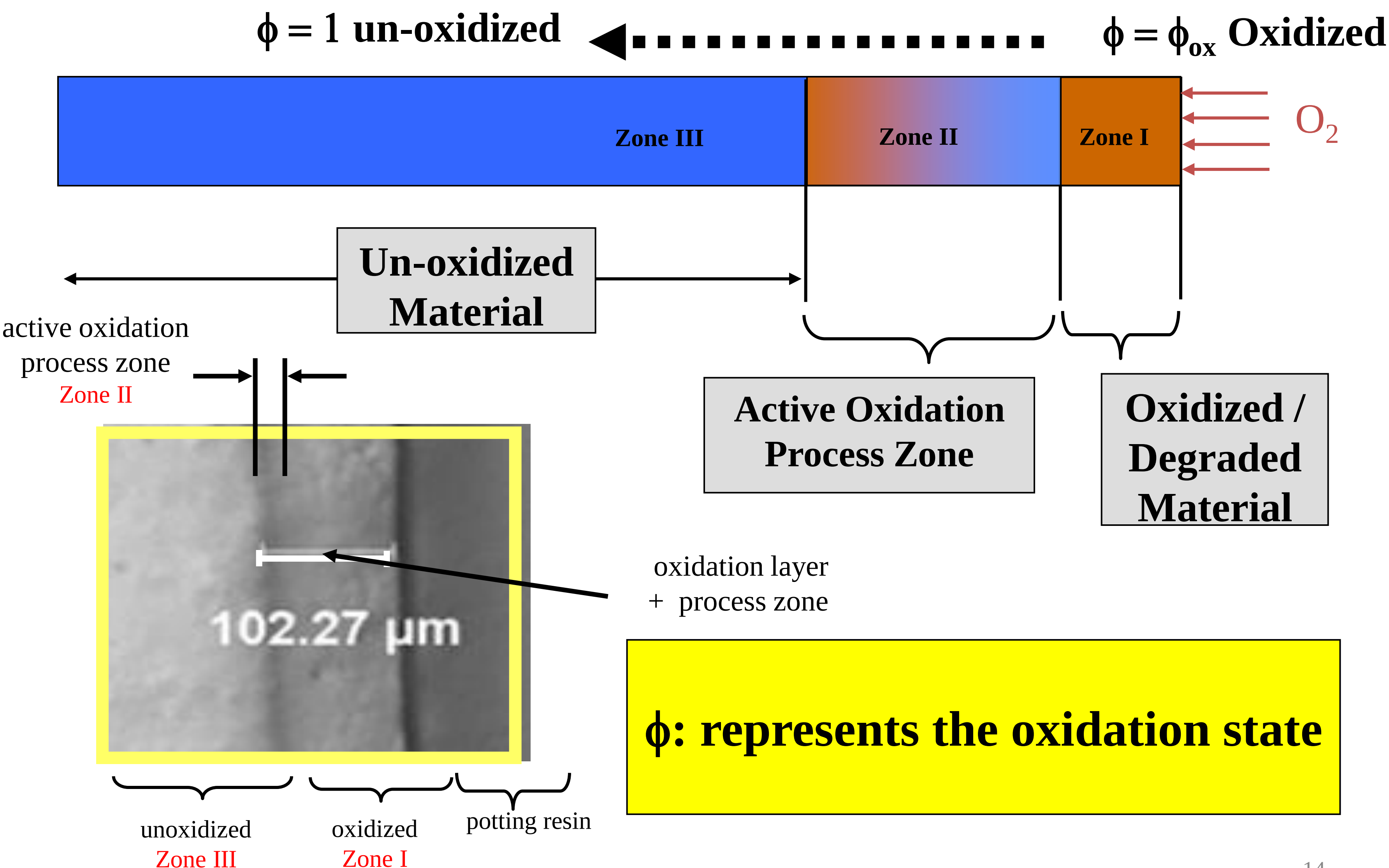


[1] Pochiraju and Tandon, JEMT, 2006; [2] Tandon, Pochiraju, Schoeppner, PDS 2006

Coupled Oxidation-Damage Mechanisms



Oxidation Model



ϕ: represents the oxidation state

Pochiraju et al., 2006

Modeling Thermo-Oxidation of Polymers

Diffusion-Reaction System

$$\frac{dC(x,t)}{dt} = D(\phi,T)\frac{d^2C(x,t)}{dx^2} - R(C,T,\phi)$$

$$C(0,t) = C^s \mathrm{mol/m^3}$$

$$\frac{dC}{dx}(L,t) = 0.0$$

$$C(x,0) \sim 0\mathrm{mol/m^3}$$

Reaction Rate Model

$$R(C,T,\phi) = R_0(T)\psi(C)\left\{\frac{\phi-\phi_{ox}}{1-\phi_{ox}}\right\}$$

$$= R_0(T)\frac{2\beta C}{1+\beta C}\left(1-\frac{\beta C}{2(1+\beta C)}\right)\left\{\frac{\phi-\phi_{ox}}{1-\phi_{ox}}\right\}$$

$$R_0(T) = R^* e^{\frac{-R_a}{RT}}$$

Conversion Model

$$\frac{d\phi}{dt} = \alpha(t)R(C)$$

$$1 < \phi < \phi_{ox}$$

$$\alpha(t) = \alpha^*(\mathrm{constant})$$

$$= \begin{cases} \alpha^1 + \alpha^2\left(\frac{t^*-t}{t^*}\right) : \mathrm{t} < \mathrm{t}^* \\ \alpha^* : t > t^* \end{cases}$$

Oxidation State Dependent Diffusivity

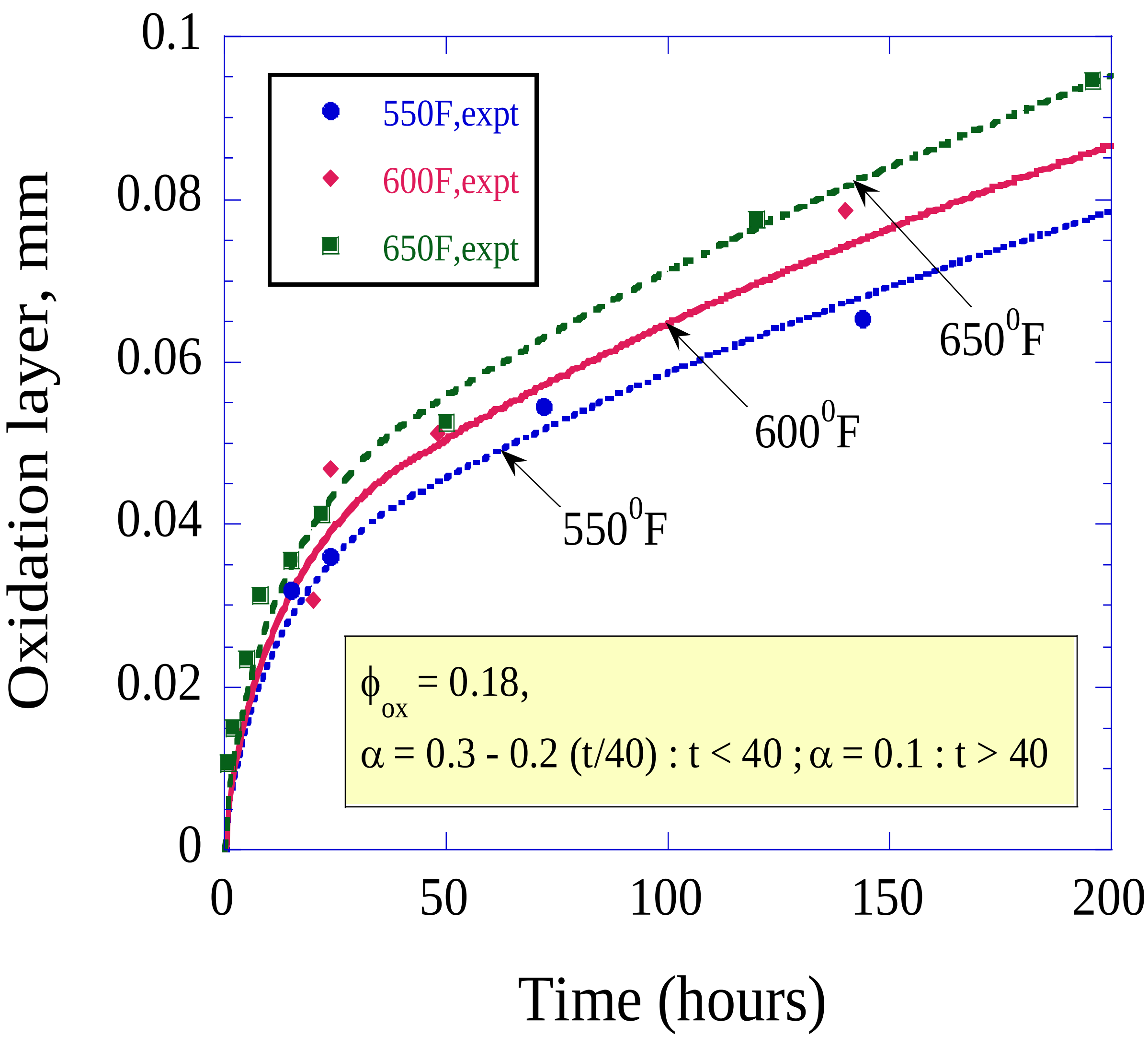
Phase(ϕ) and Temperature (T) Dependent

$$D_{ij}(\phi,T) = D^{un}(T)\left(\frac{\phi-\phi_{ox}}{1-\phi_{ox}}\right) + D^{ox}(T)\left(\frac{1-\phi}{1-\phi_{ox}}\right)$$

$$D^{un}(T) = D^*_{un} e^{\frac{-E_a^{un}}{RT}}$$

$$D^{ox}(T) = D^*_{ox} e^{\frac{-E_a^{ox}}{RT}}$$

Oxidative Layer Growth in PMR-15



Pochiraju, Tandon, Schoeppner, JEMT 2006

Stress-Coupled Diffusion-Reaction Modeling

RATE OF CHANGE OF O_2 CONCENTRATION

Stress-coupled Diffusivity and

REACTION OR CONSUMPTION TERM

$$\frac{\partial C(x,t)}{\partial t} = \underbrace{[D(\phi,T)+N\mathrm{e}]\nabla^2 C(x,t) - (M-N)\nabla \mathrm{e}\cdot\nabla C(x,t)} - R^*(C(x,t),\emptyset)$$

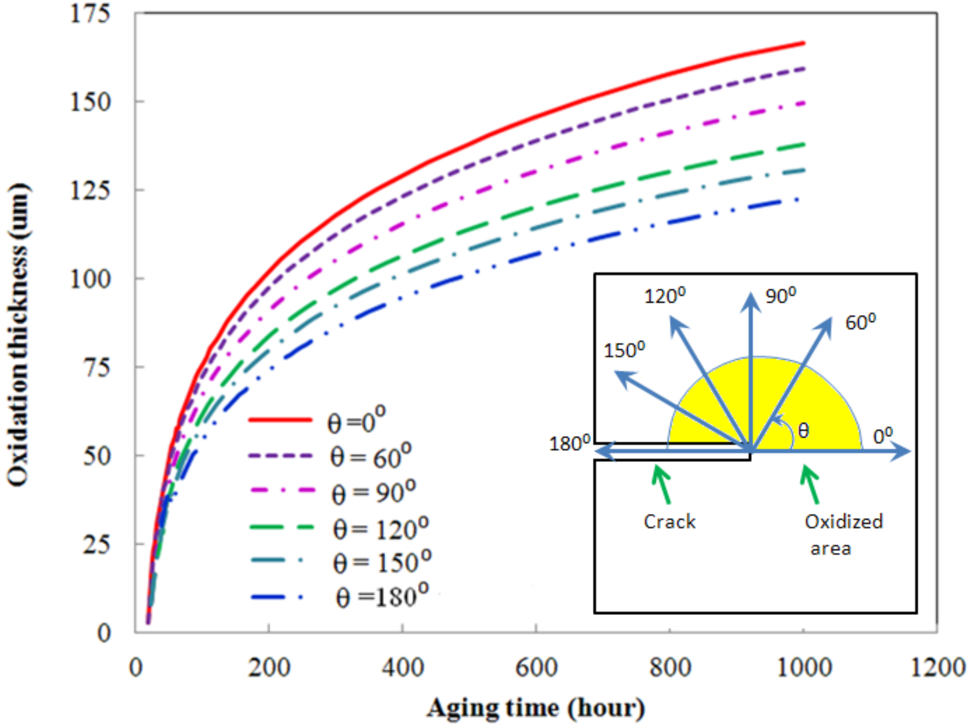
Boundary Sorption = Solubility × Partial Pressure O_2 → $C_S = SP_{O_2}$

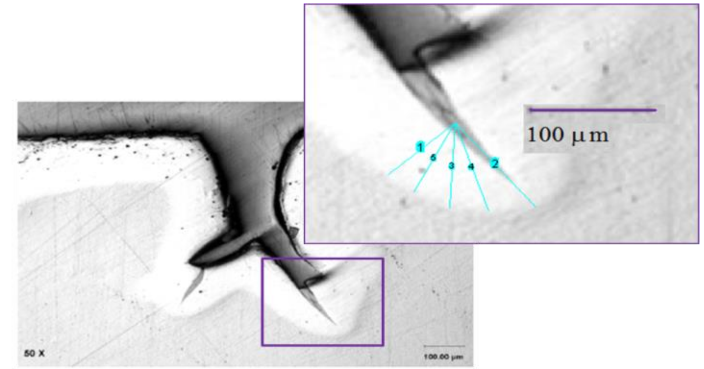
Periodic/Symmetric Boundary conditions → $\nabla C.\, n = 0$

Diffusivity Assumed to obey Arrhenius Law → $D_{ij} = D_{ij}^0 \exp\left(-\frac{E_a}{RT}\right)$

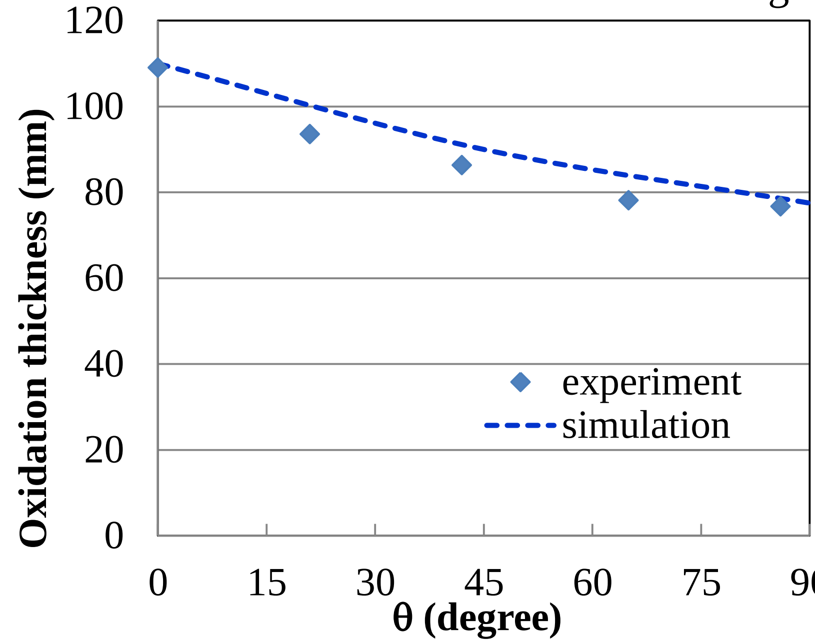
Oxidation in the Vicinity of Cracks

Oxidation growth at the crack tip in BMI resins



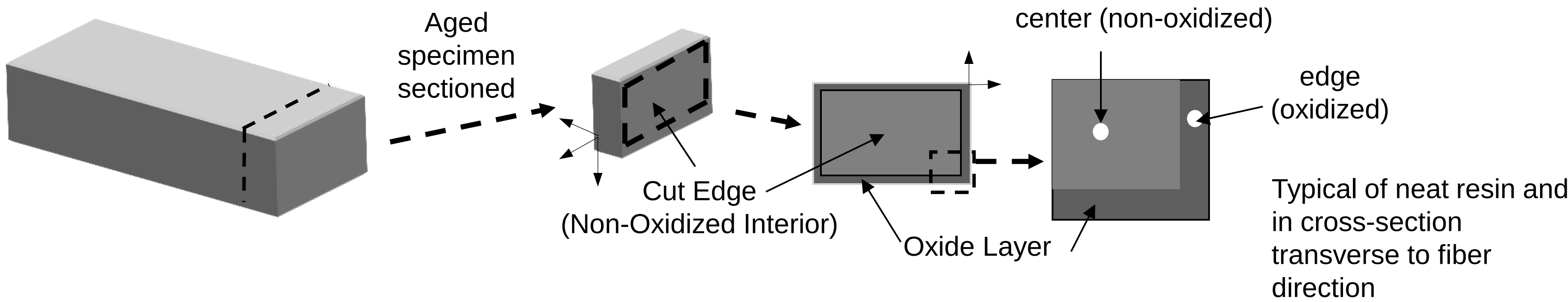


Oxidation thickness vs. orientation angle



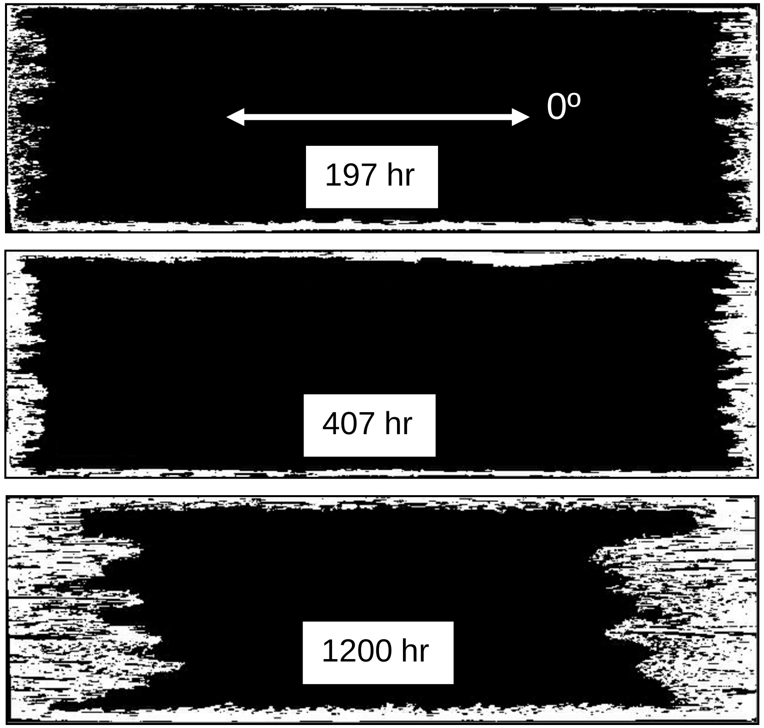
Angular variation of stress correlates to the oxidation depth around cracks

Oxidation of Unidirectional Lamina

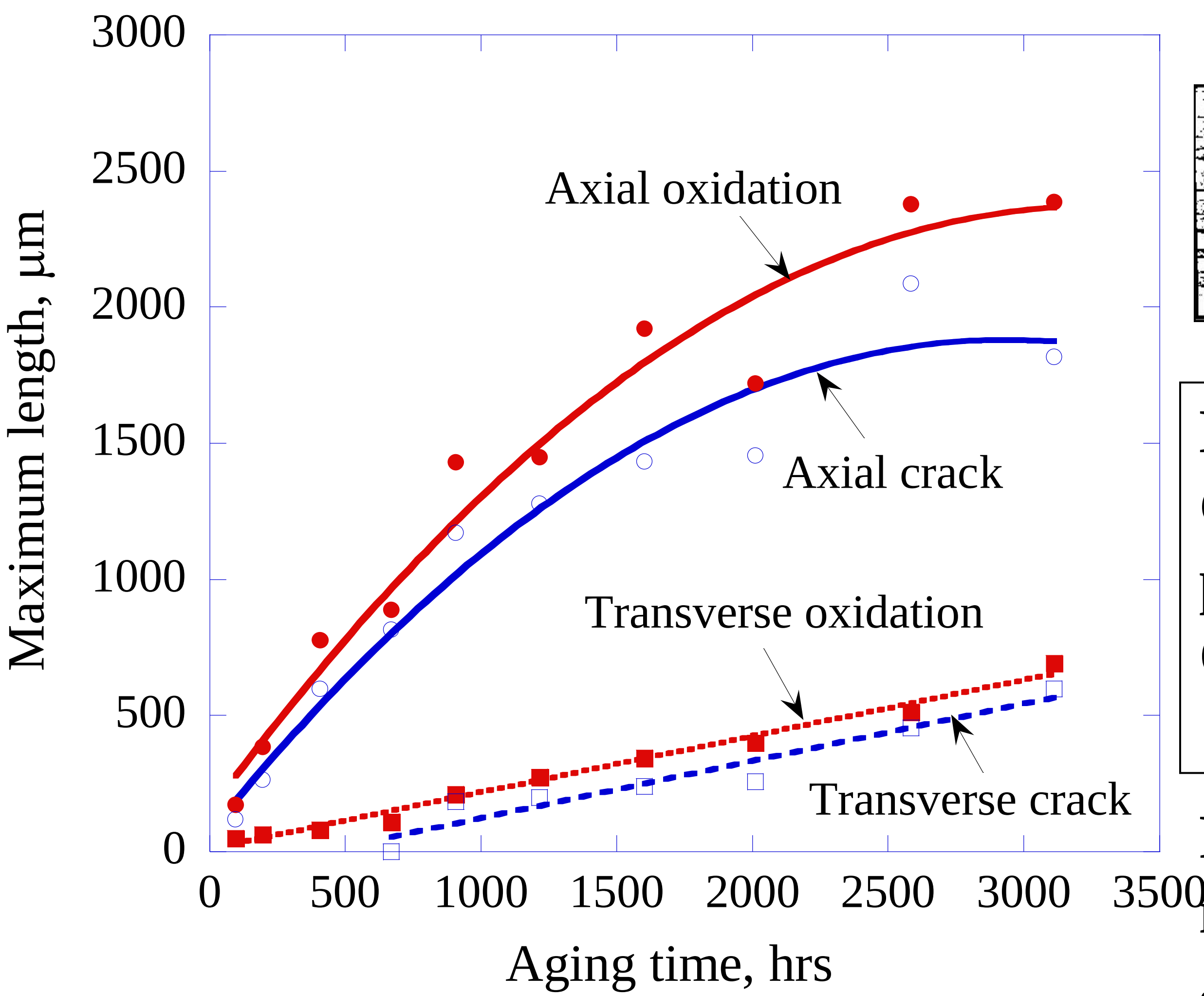


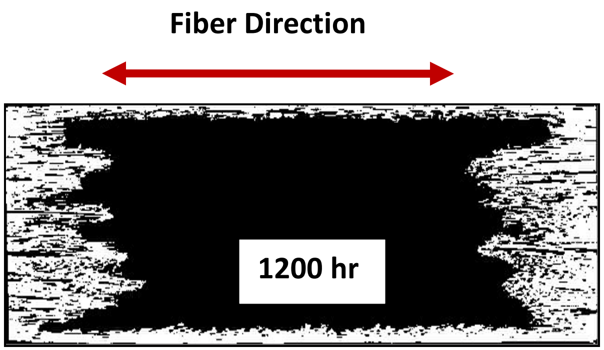
Unidirectional G30-500/PMR-15 aged at 288ºC

- Oxidized resin becomes lighter in color
- Development and growth of voids and microcracks into surface
- **<u>Preferential oxidation in axial direction</u>**



Fiber Orientation Dependent Oxidation





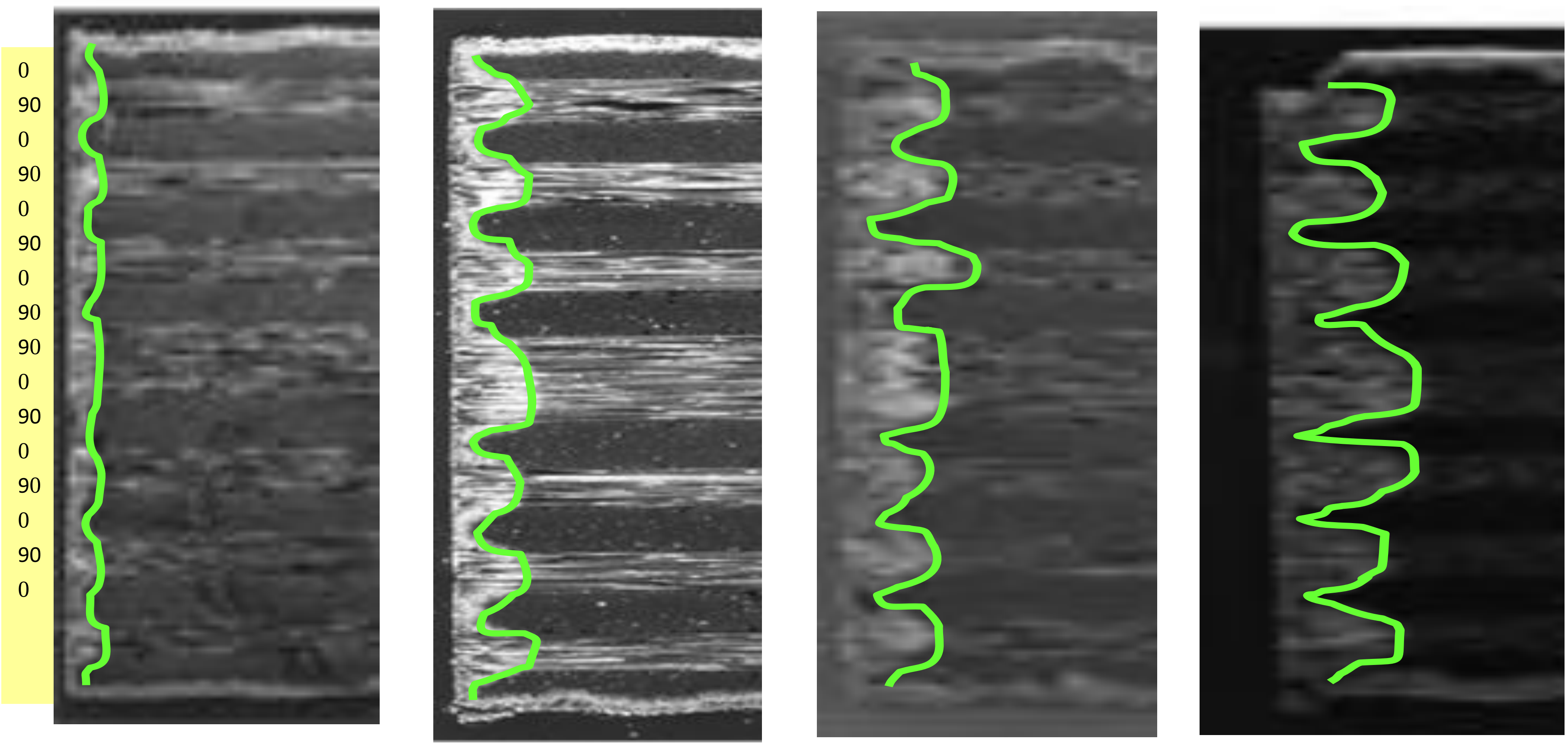
Both Oxidation Growth and damage propagation are Orthotropic

Penetrates deeper into the laminate along fiber direction

Pochiraju & Tandon (2009) *Composites Part A: App. Sci. and Manuf.*

Heterogeneous Laminate Behavior
Cross-ply laminate, $[0/90]_{4s}$

View is of cross-section perpendicular to 0º direction



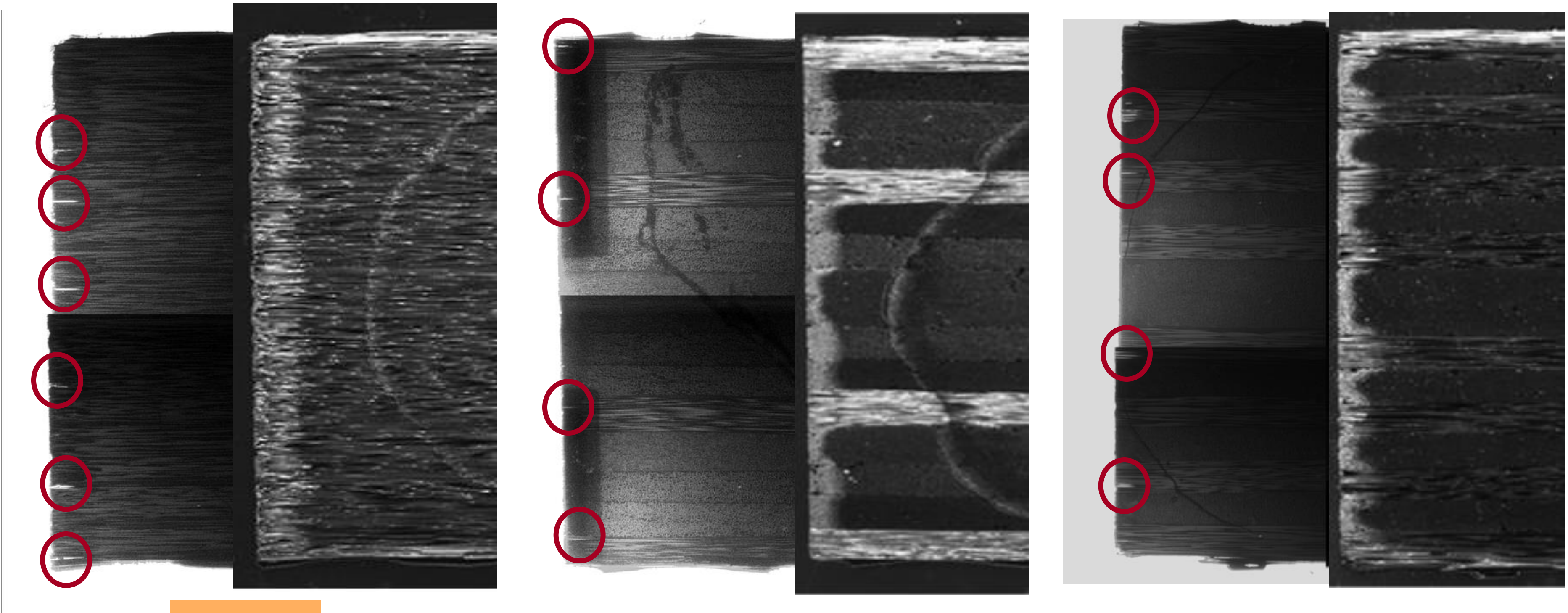
250 hr 750 hr 1500 hr 2000 hr

- Preferential oxidation growth along the fiber paths for the cross-ply laminate
- Maximum/minimum oxidation extent occur at the plies midplane

Tandon & Pochiraju (2010) ***J. Composite Materials***

Oxidation of Laminates

750 hr

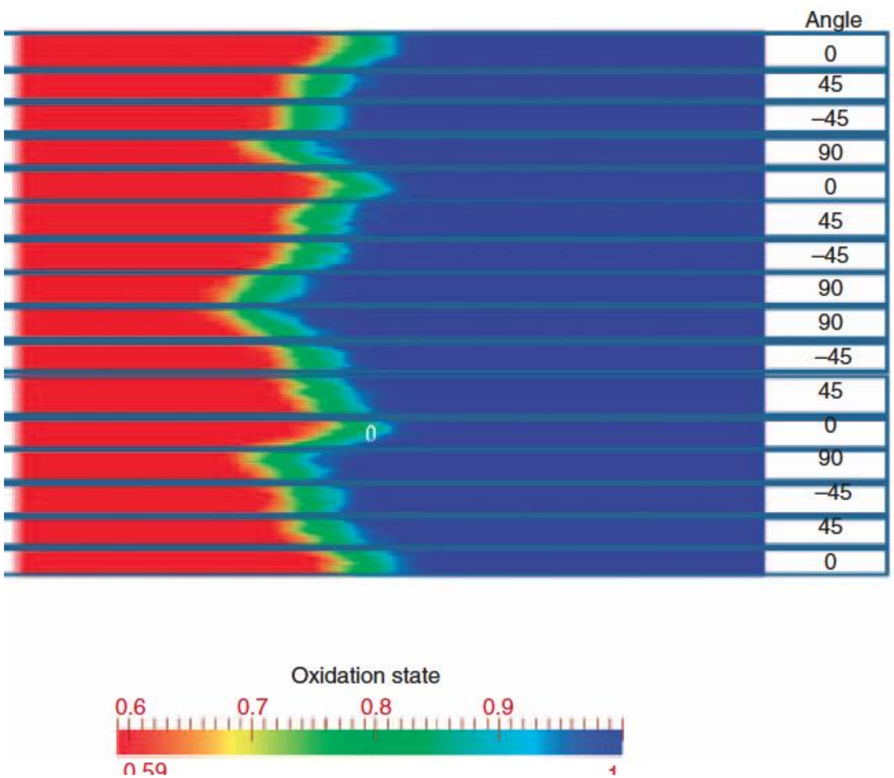


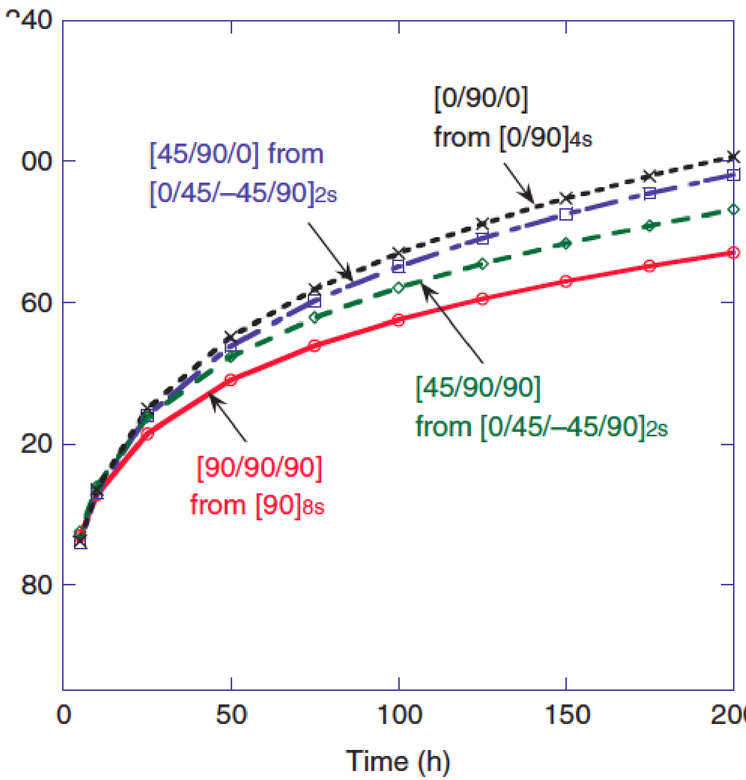
$[0]_{16t}$ $[0/45/-45/90]_{2s}$ $[0/90]_{4s}$

- Short fiber matrix debonds along the 0º fiber direction
- Oxidation has advanced to a greater extent in the region of the specimen corresponding to the location of the debond cracks

Parallel to 0 degree direction

Modeling Oxidation of Laminates (No Damage)

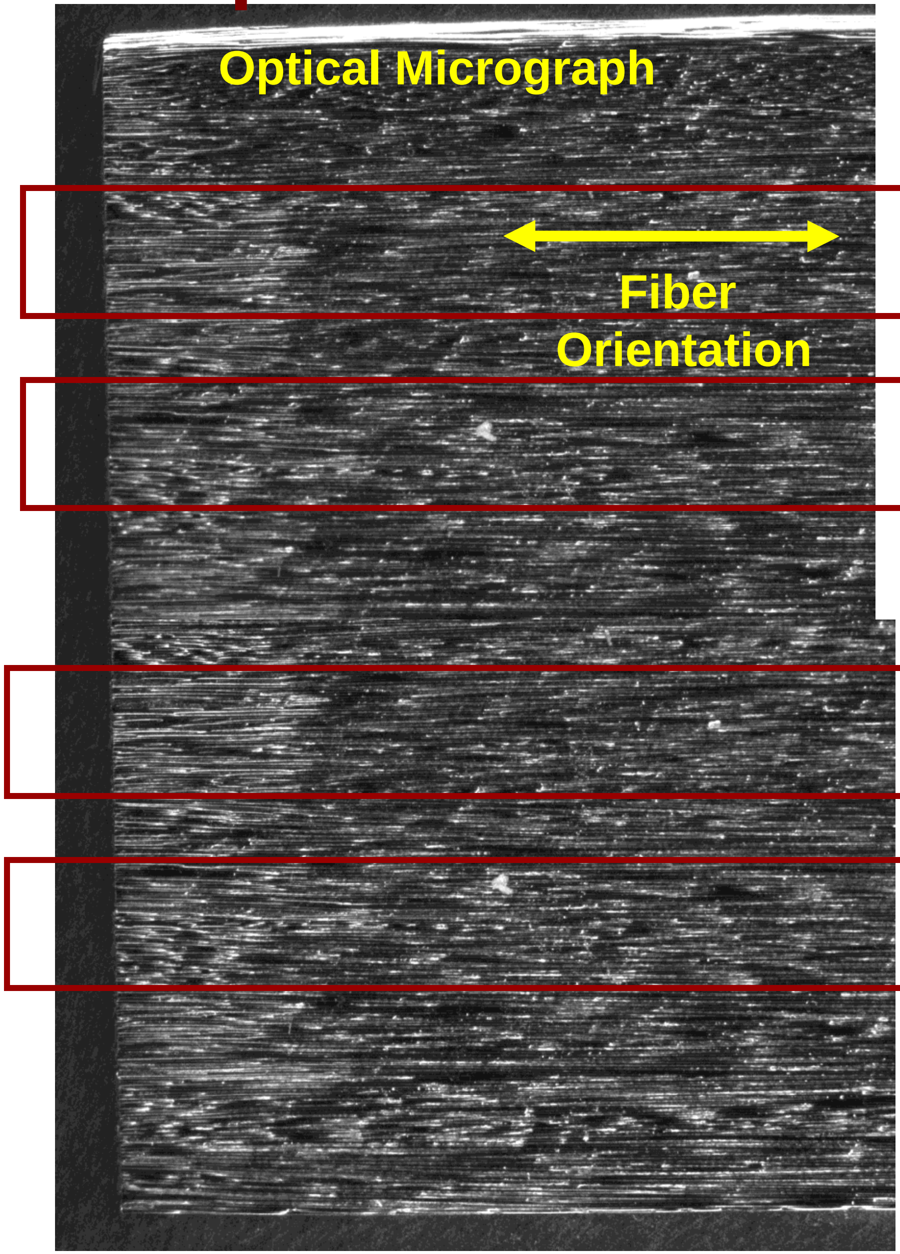


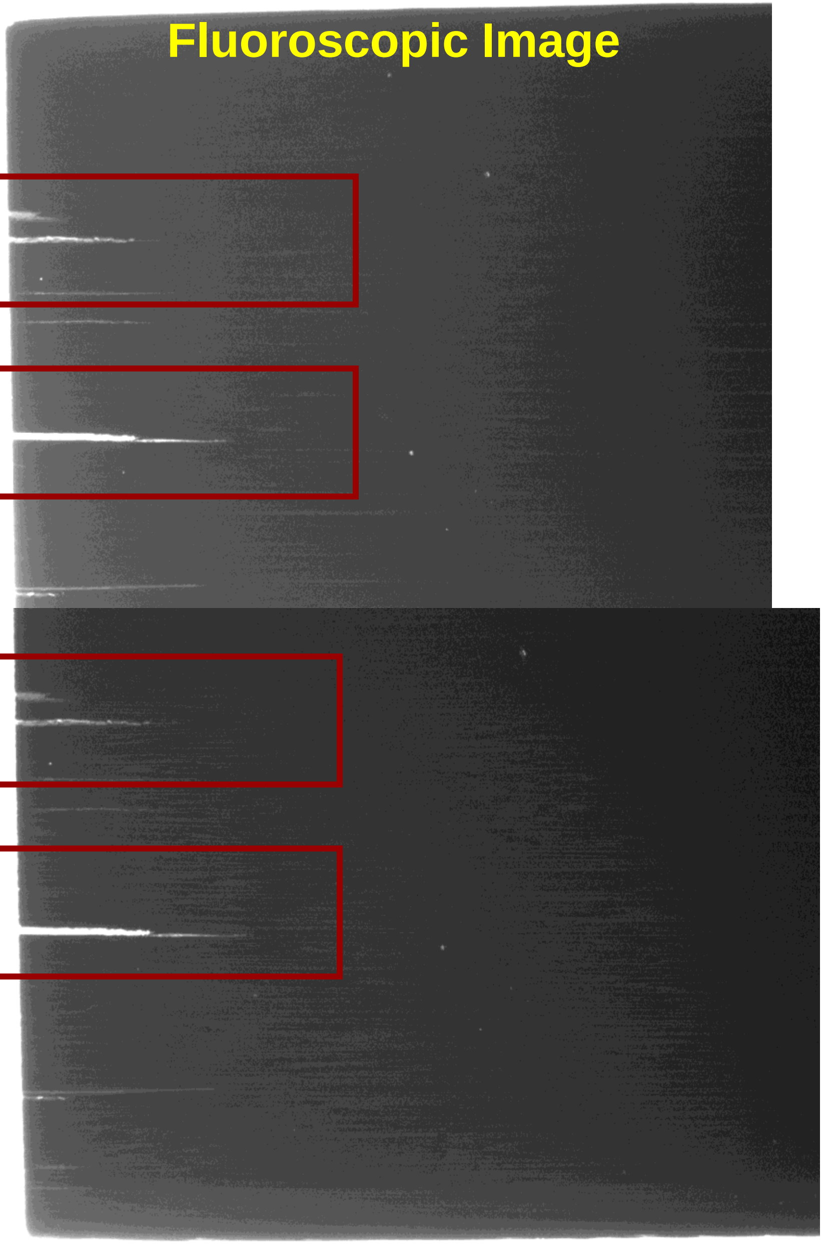


- Anisotropy can be effectively modeled **in areas without damage**
- Requires 3D simulations and orthotropic diffusivity tensor
- Most effects are confined to adjacent plies

Tandon & Pochiraju, JCM, 2011

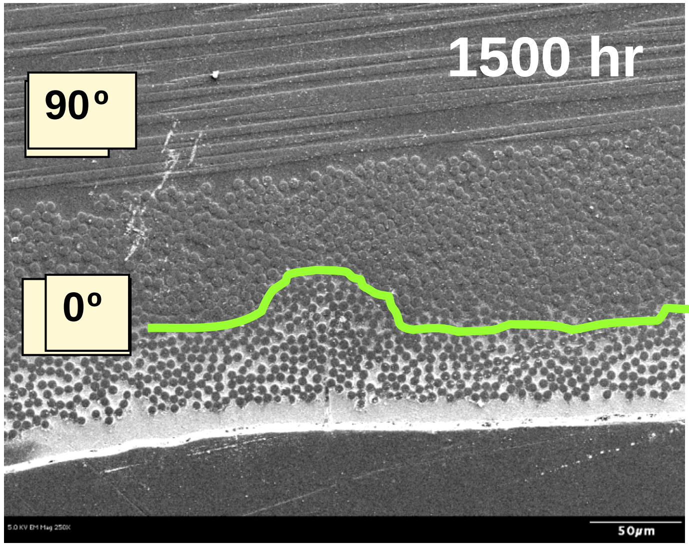
Optical and Fluoroscopic Imaging

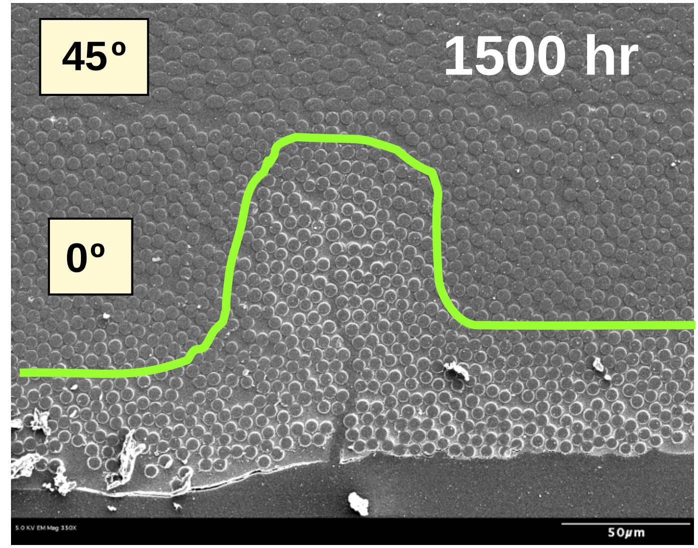


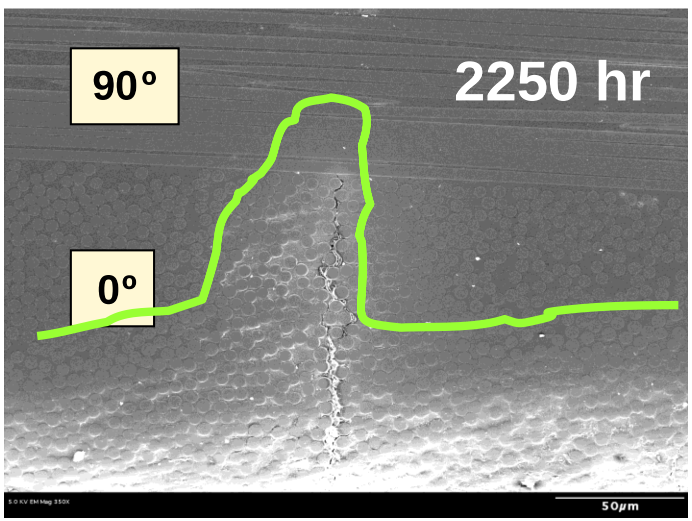


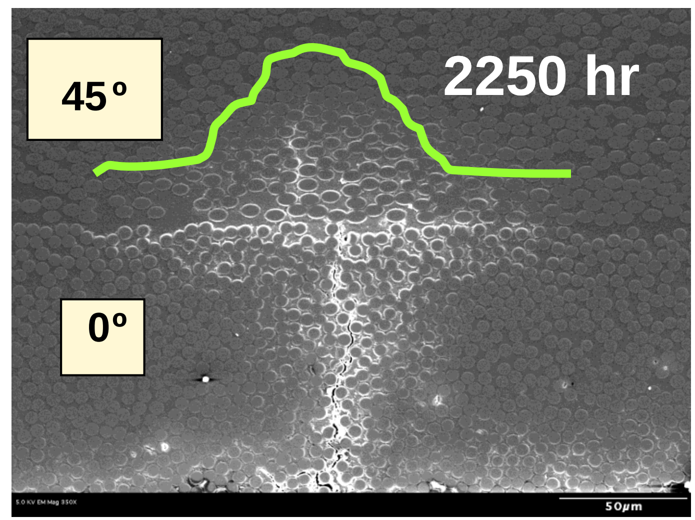
Aged at 288 °C 405 Hours

Thermal-Oxidation in Laminates





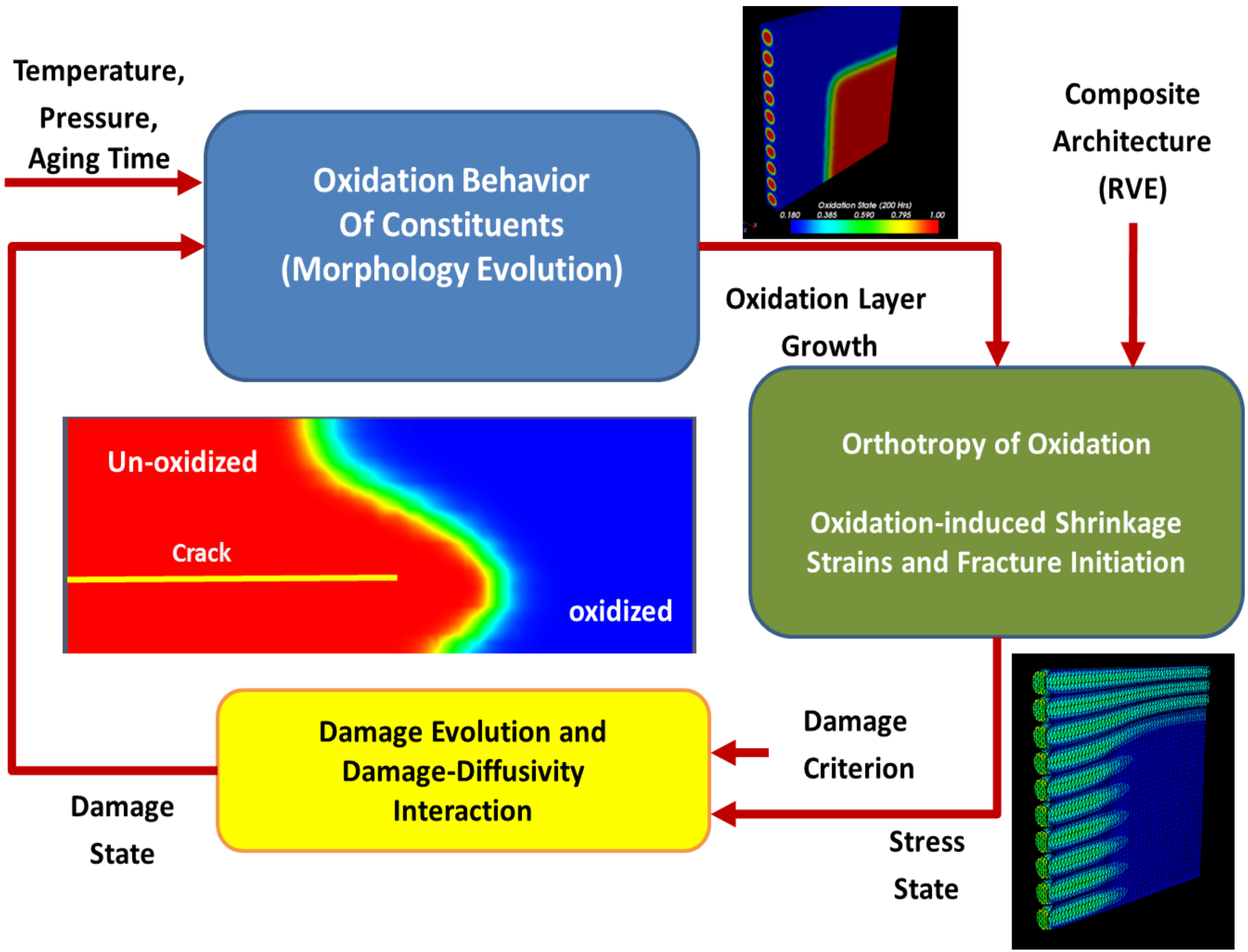




$[0/90]_{4S}$

$[0/\pm45/90]_{2S}$

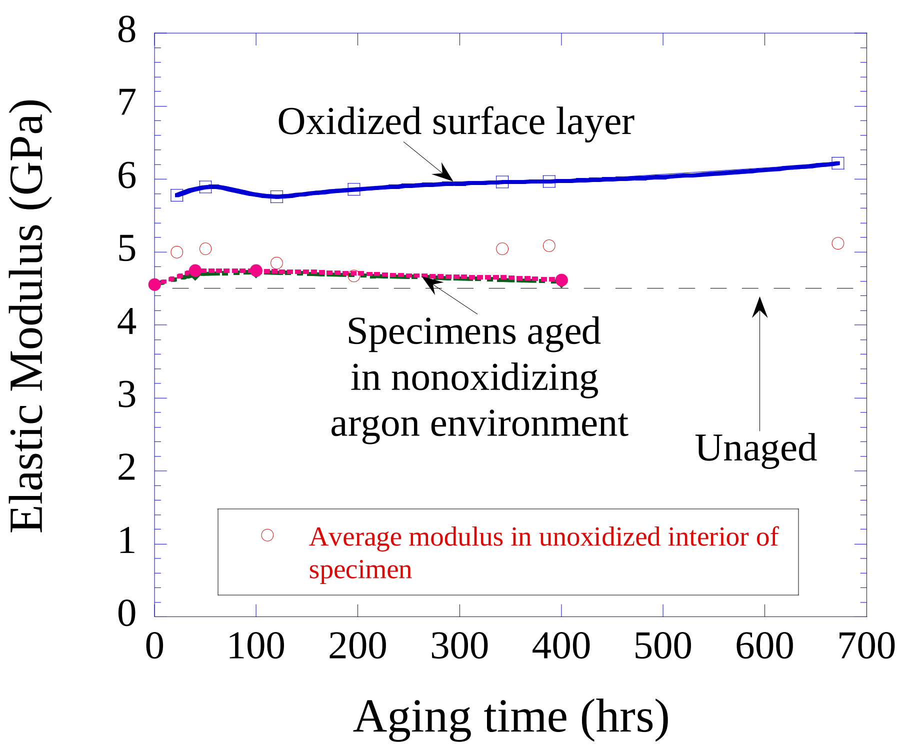
Coupled Oxidation-Damage Scheme



Oxidation induces Shrinkage Strains

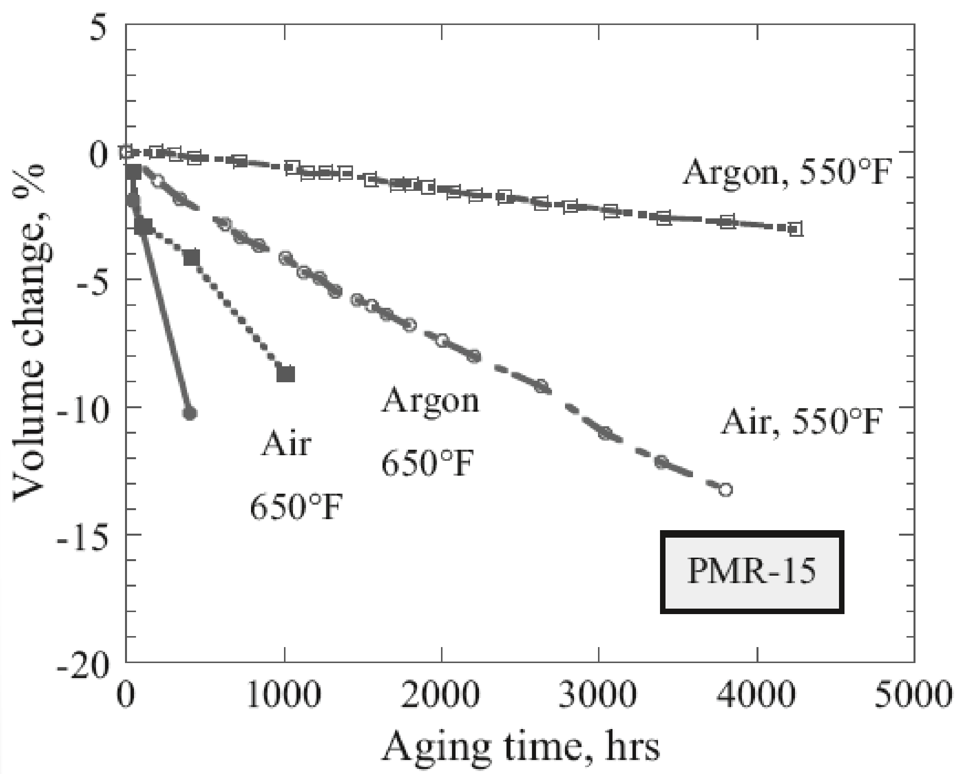
Micromechanical effects due to morphological changes

Modulus Changes



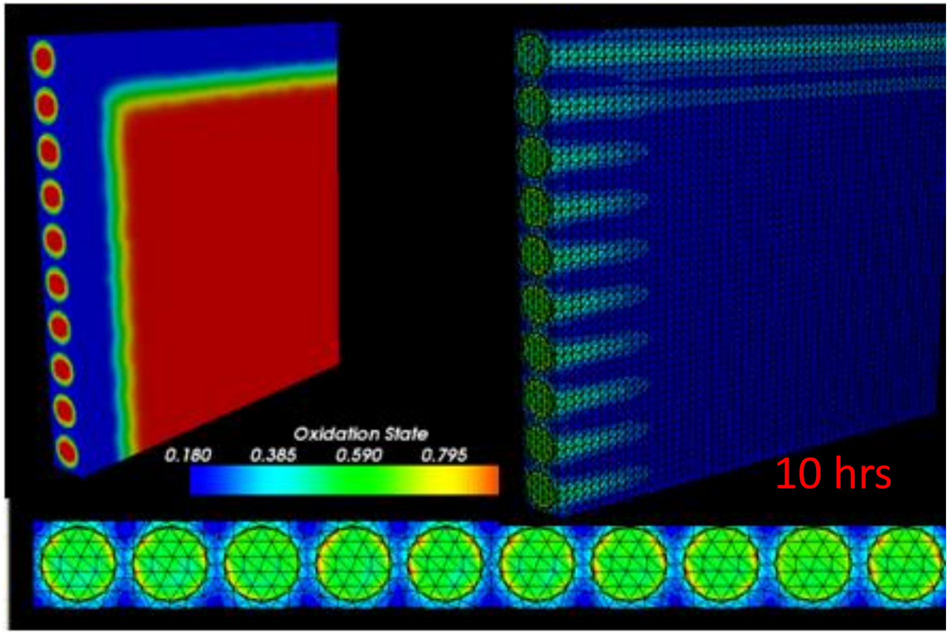
$$E(\varphi,T) = E_{un}(T)e^{\left(K_{ox}\frac{1-\varphi}{1-\varphi_{ox}}\right)}e^{\left(K_{nox}\frac{\varphi-\varphi_{ox}}{1-\varphi_{ox}}t\right)}$$

Resin Shrinkage



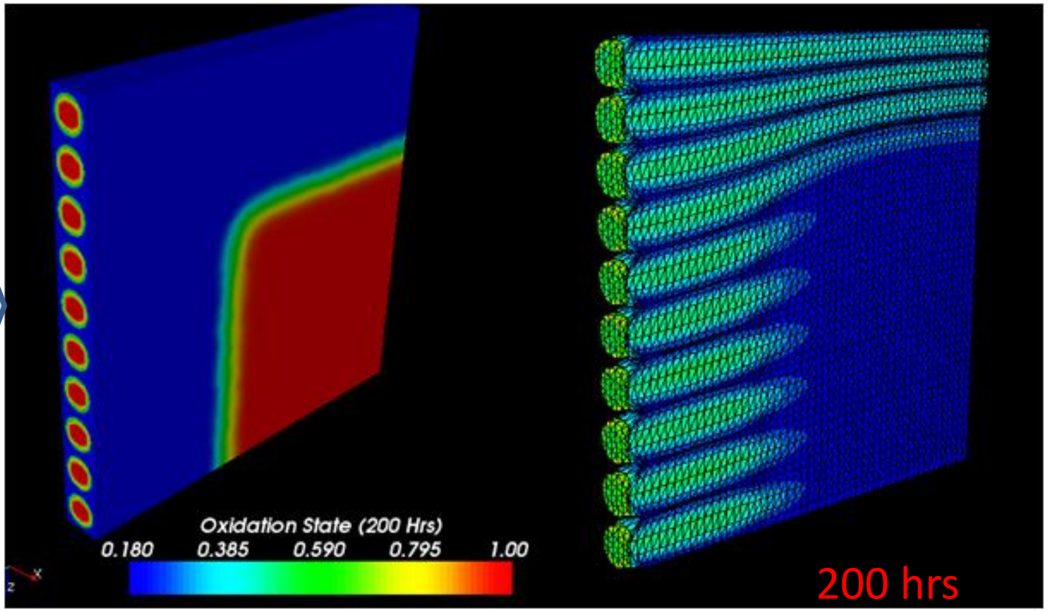
$$\beta(\phi,t,T) = \beta_\phi(T)\frac{\phi-\phi_{ox}}{1-\phi_{ox}} + \beta_t(T)t_a$$

Evolution of Stress During Oxidative Aging

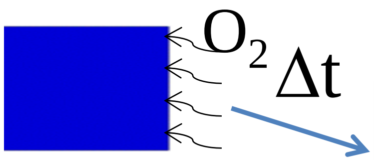


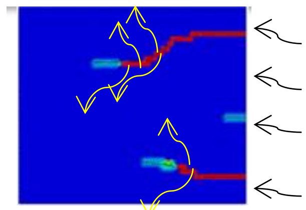
- Oxidation Layer (Left) and stress fields (right) after 10 Hours of aging.
- The peak Von Mises effective stresses (2.4 MPa) are at the fiber matrix interface and free edge (below)
- Average interstitial matrix stresses are at 0.4 MPa and in fiber is 2.4 MPa

- Oxidation Layer (left) shown at 200 hours
- Peak stress on the free edge is 47.3 MPa
- Average interstitial matrix stresses are at 1.2 MPa
- Average fiber stress = 25 MPa
- Matrix strength ~ 41MPa @288 C



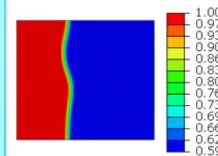
Coupled Oxidation & Damage Model





Oxidation Model

Diffusion-Reaction Equation
Orthotropic Diffusivity
Surface Absorption on Boundary and Crack Surfaces by Henry's Law
Galerkin FEM, JCG Technique
Output: Oxidation State ∅



Oxidation state
0.59 fully oxidized
1.0 unoxidized

φ

∅

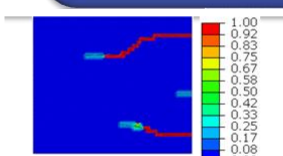
Damage Model

Progressive Damage Method
Damage Initiation Criterion
Damage Evolution
Traction-Separation Law
Output: Damage State φ and crack surface location

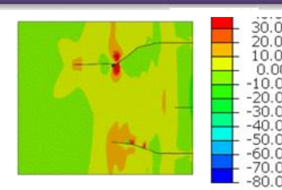
σ

Mechanics Model

Oxidation-Induced Shrinkage
Representative Volume Element
Periodic Boundary
Constitutive Relation
Output: Stress State σ



Damage state
0.0 -no damage
1.0 -fully damaged



Stress state (MPa)

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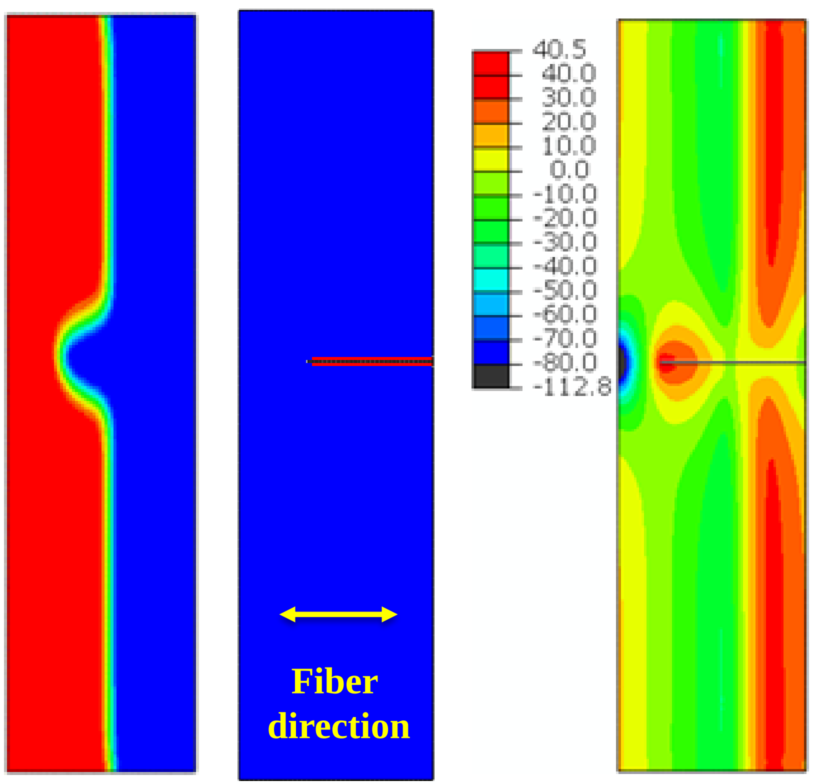
Oxidation and Damage States in a Lamina

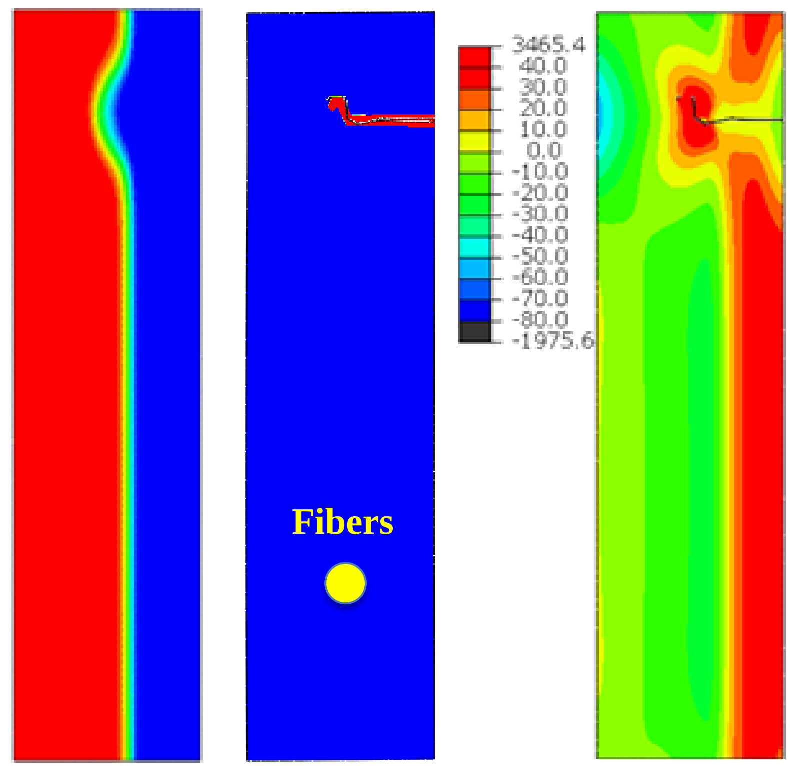
Along the fiber (axial)



ϕ d $\sigma_{yy}(MPa)$

Time = 900 Hrs

Transverse to fiber (axial)



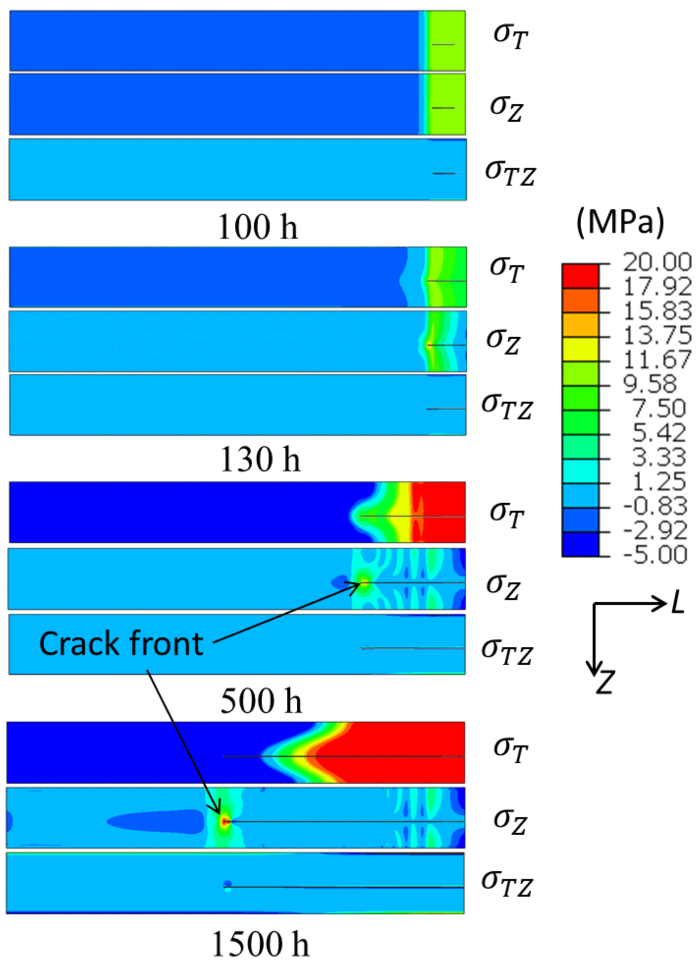
ϕ d $\sigma_{yy}(MPa)$

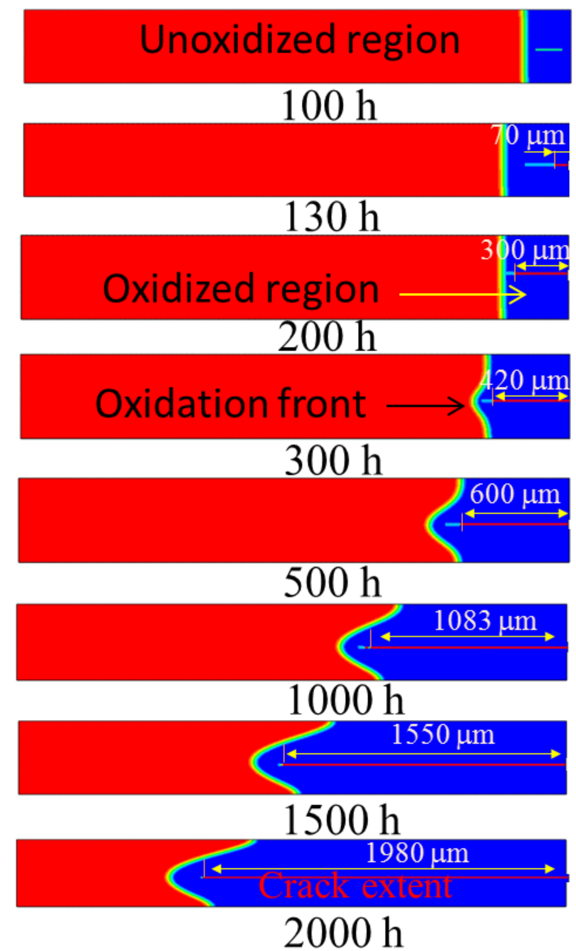
Time = 1700 Hrs

Low Toughness – Faster Crack/oxidation growth

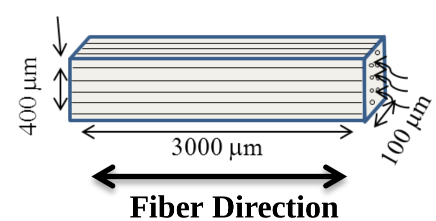
Liang & Pochiraju, 2014

Axial Oxidation and Damage Growth





Oxidation and damage evolution simulation
for a G30/PMR-15 lamina in the axial (fiber) direction



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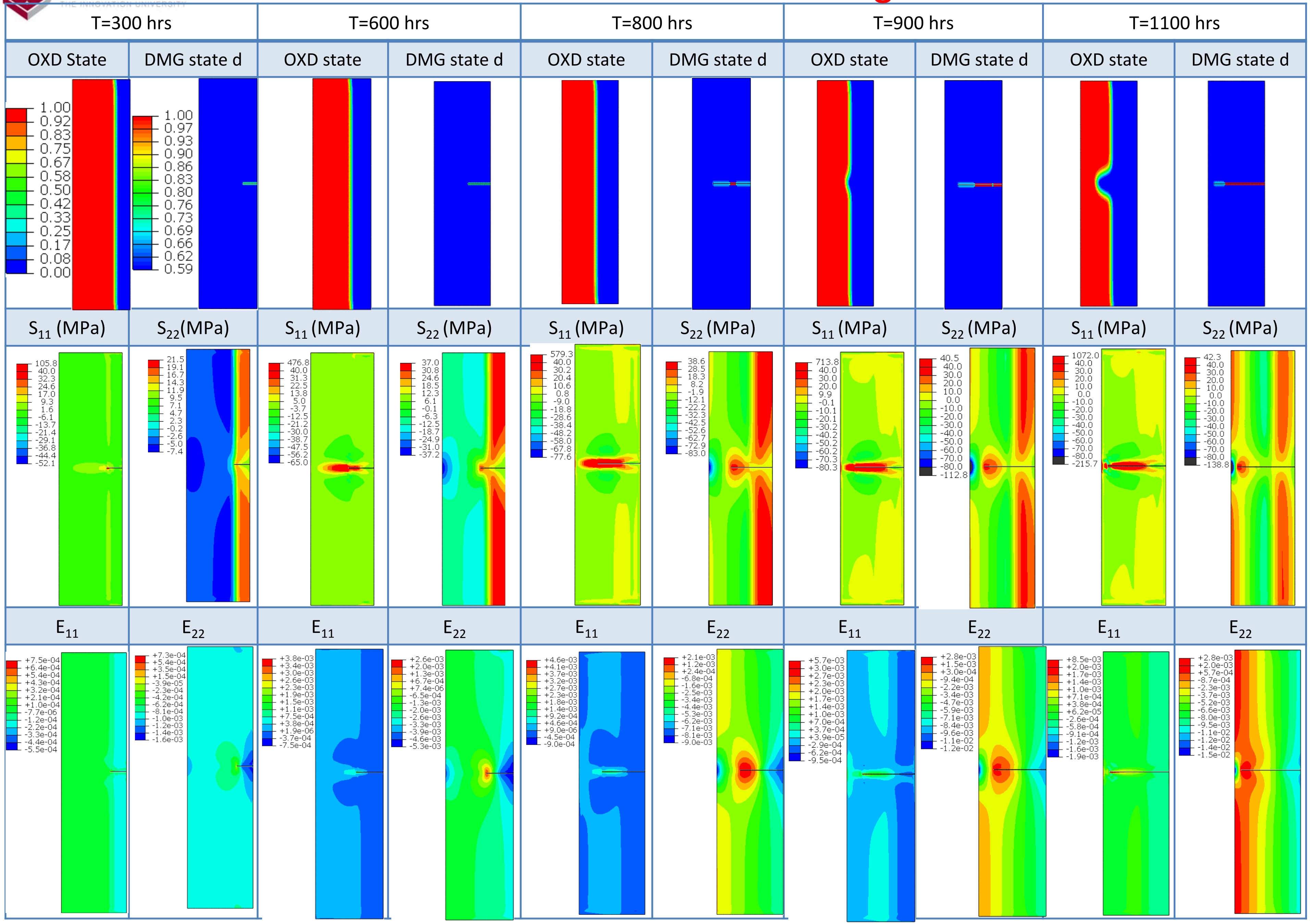
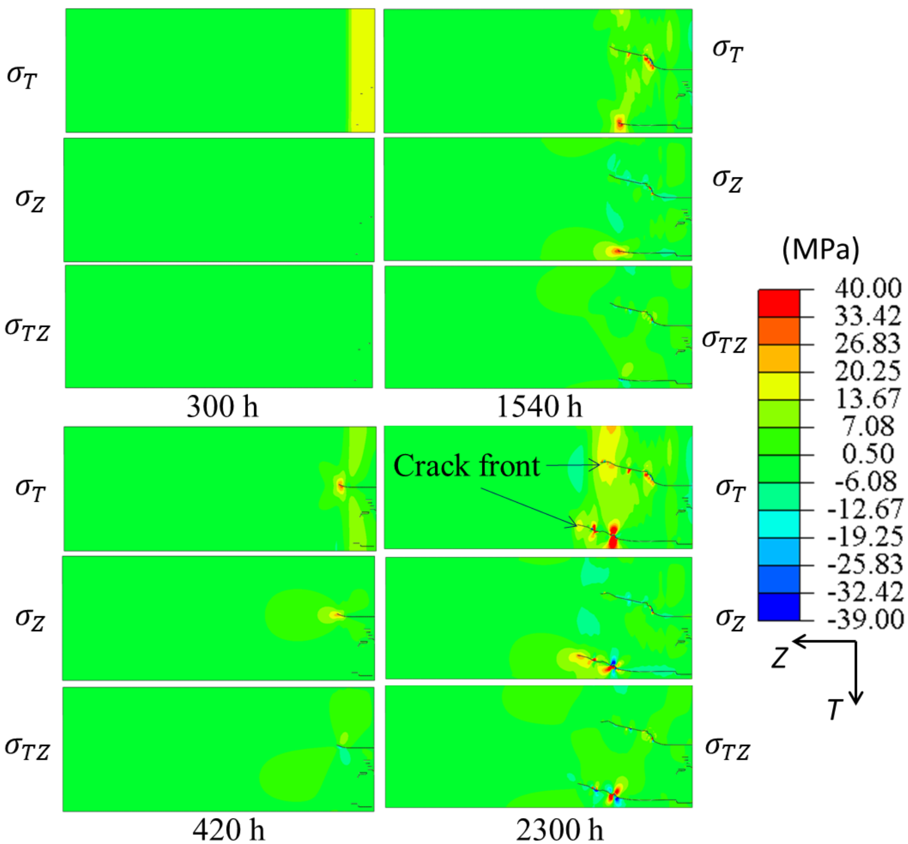
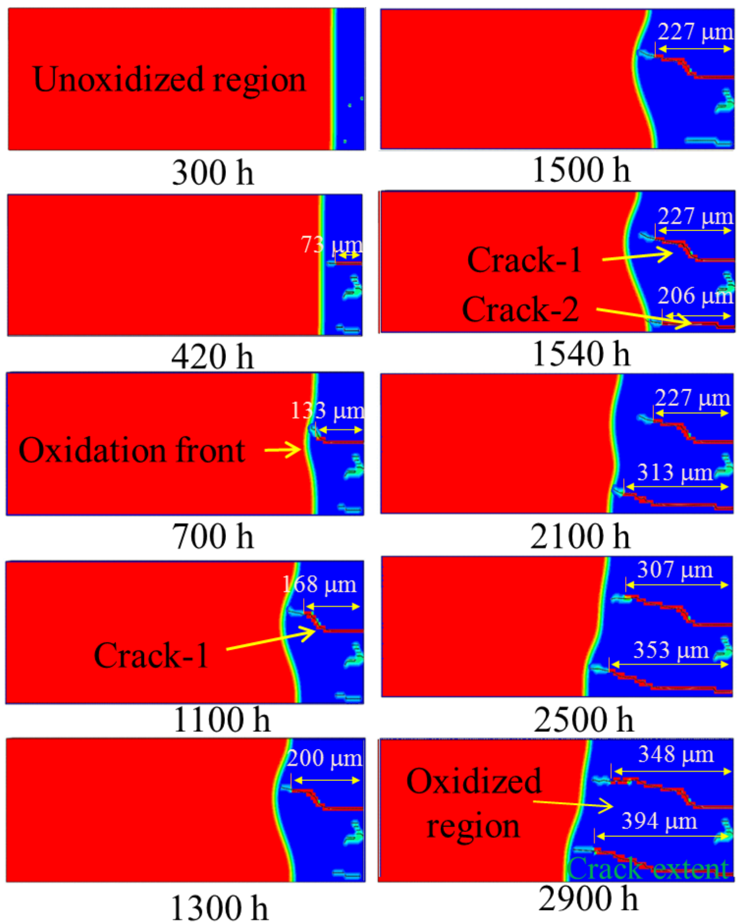
Axial Oxidation and Damage Growth

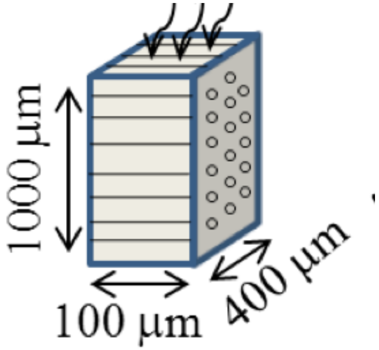


Transverse Oxidation and Damage Growth





Oxidation and damage evolution simulation for a G30/PMR-15 lamina in the transverse direction



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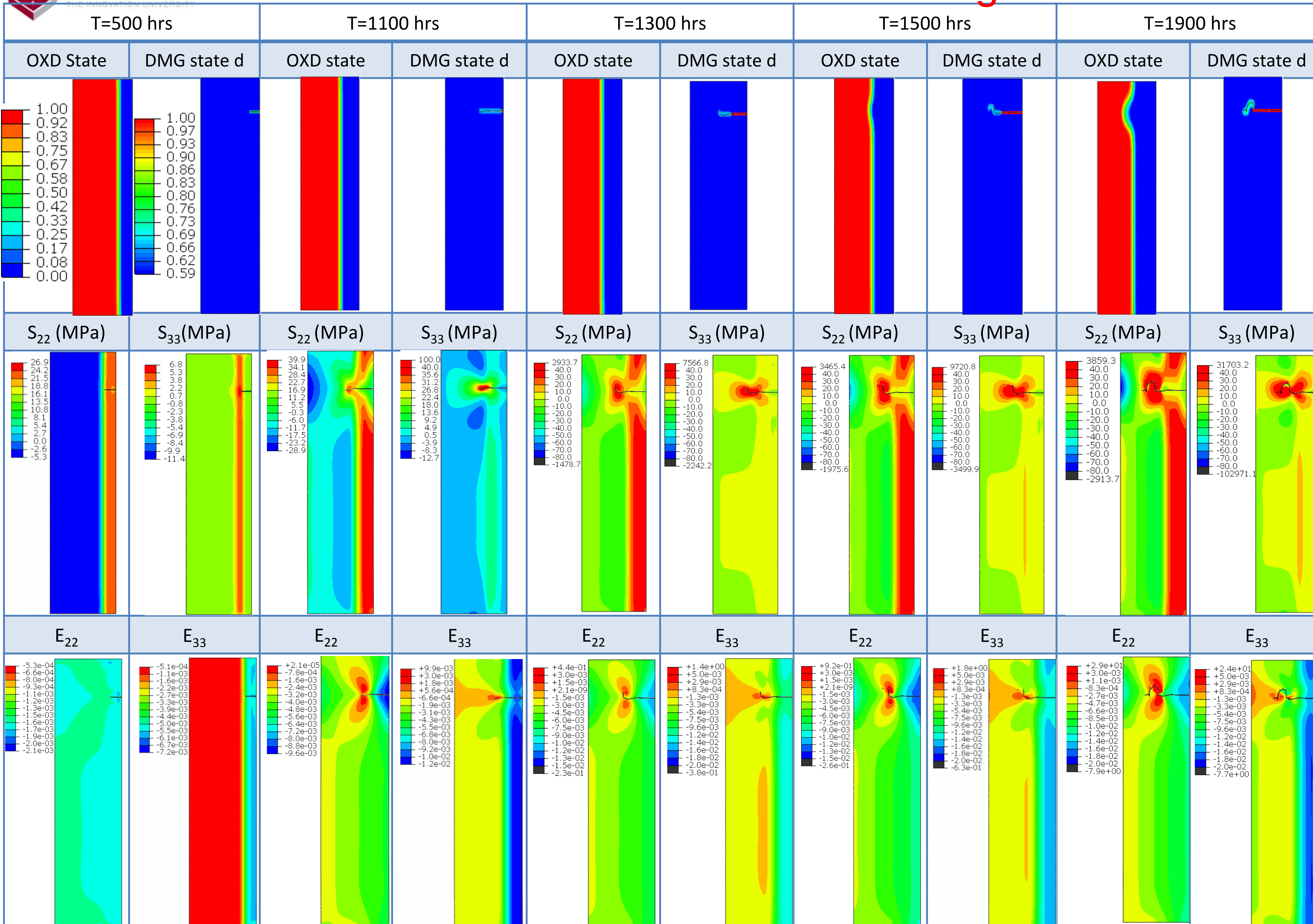
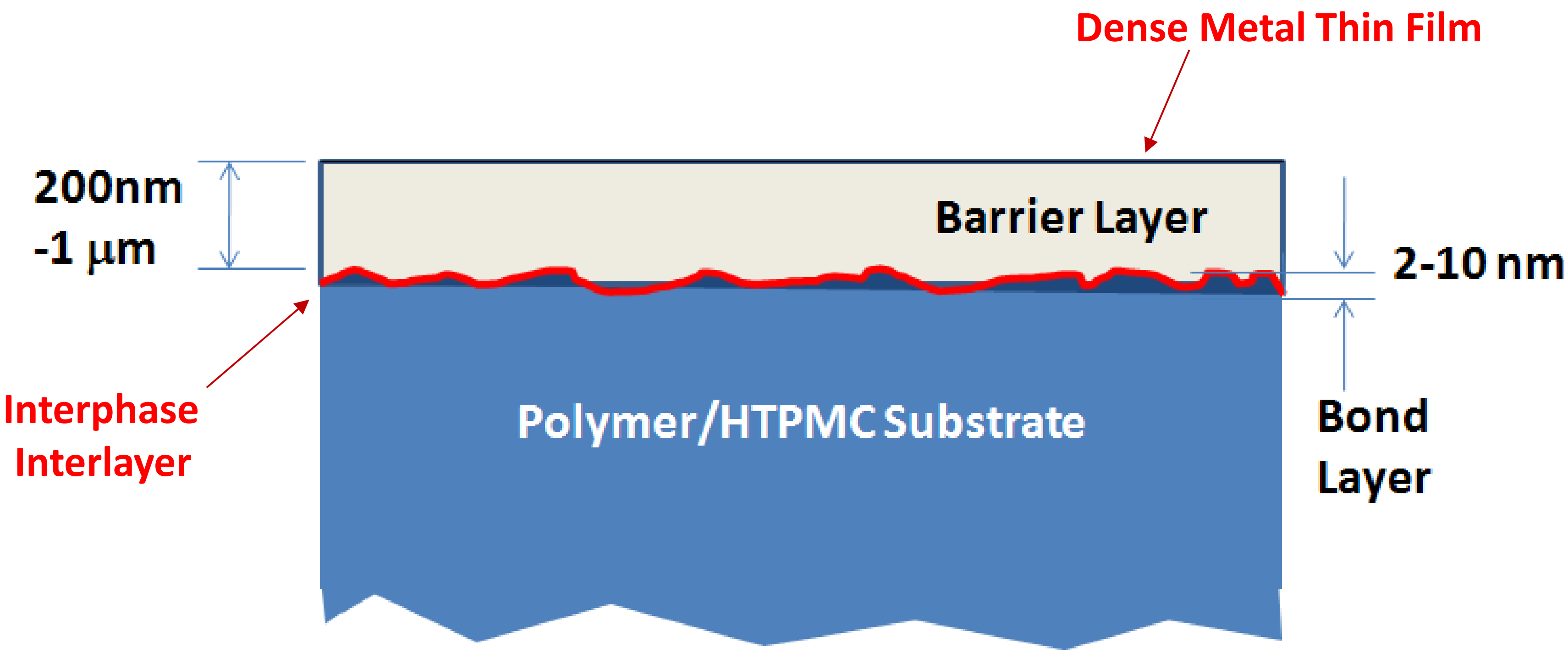
Transverse Oxidation and Damage Grwoth



Coating Morphology & Materials



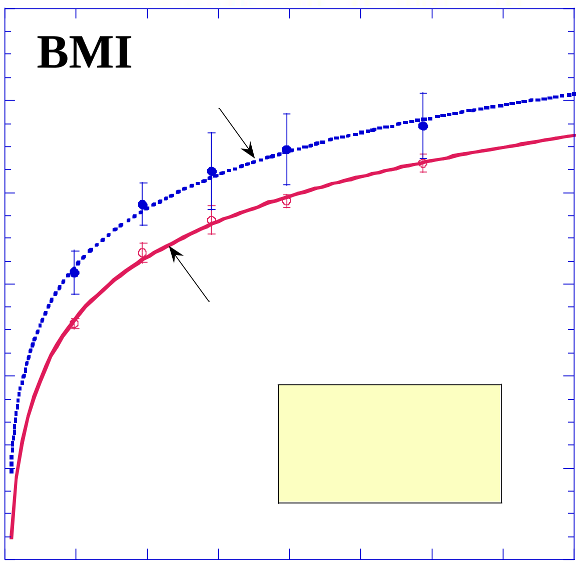
Nan, Tandon & Pochiraju, 2012

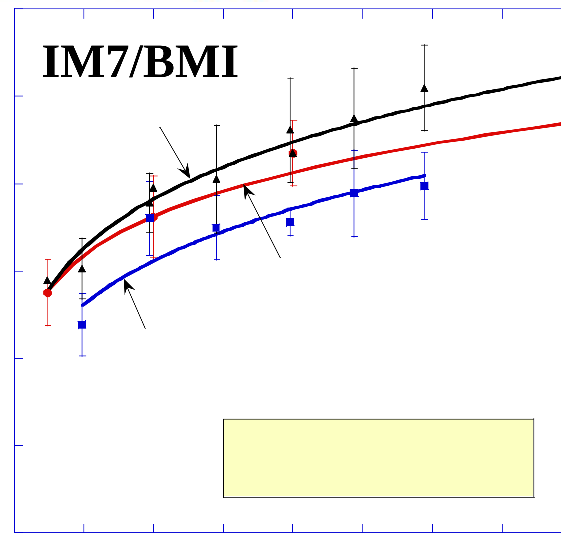
Bismaleimide with Ag Coating with Cr interlayer < 10 nm

198 hrs

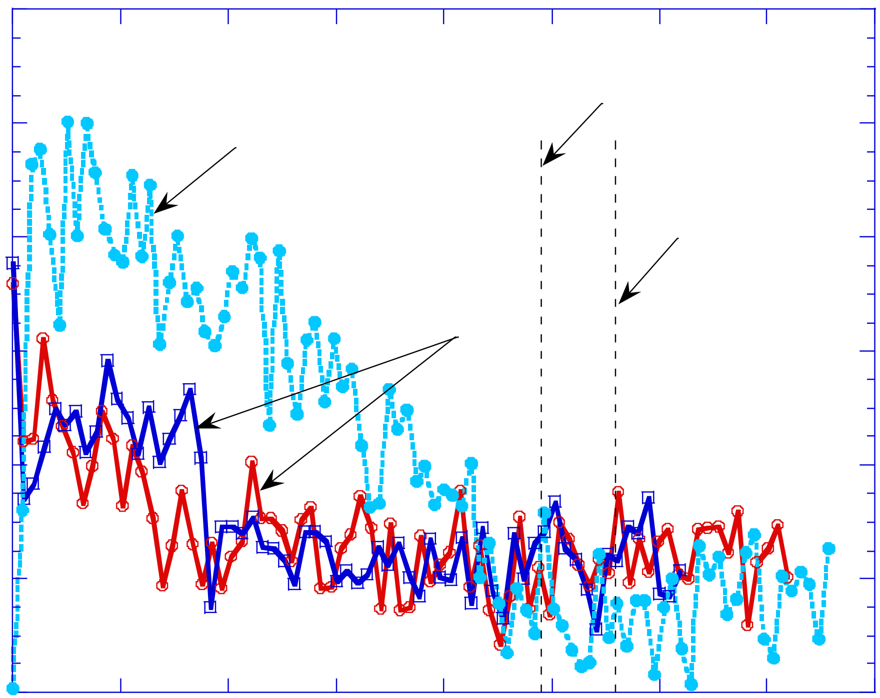
Average oxidation thickness on coated surface = 78.11 ± 1.4 µm

Average oxidation thickness on uncoated surfaces = 89.32 ± 7.64 µm



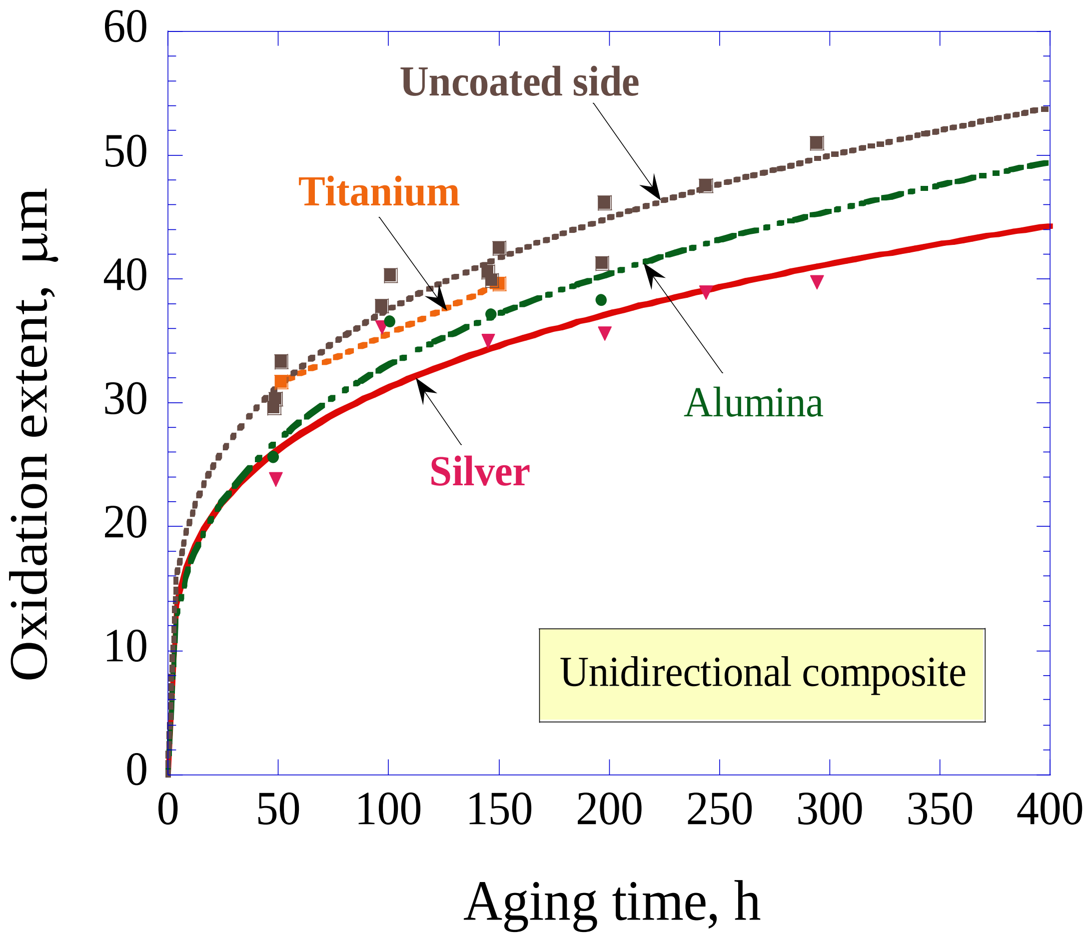


Oxidation Layer Characterization
Chemical Depth Profiling with EDAX



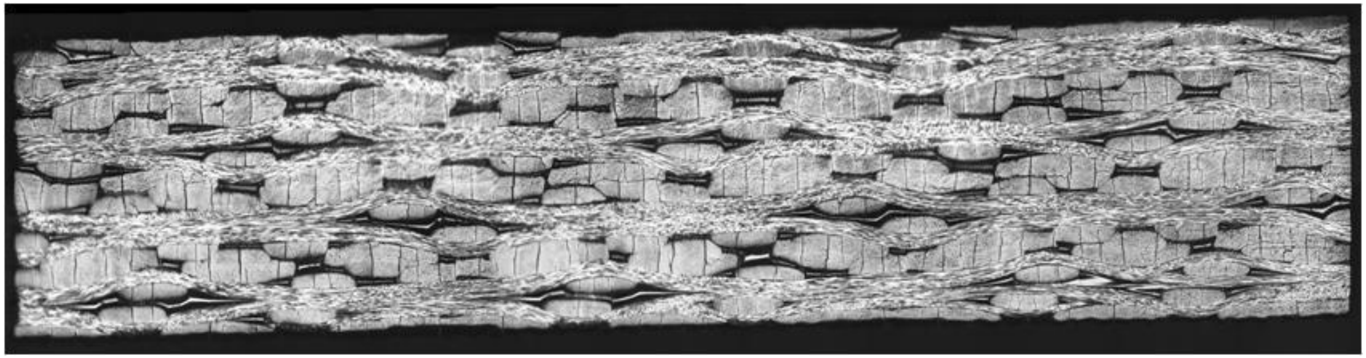
- Ratio of Oxygen to Carbon is monitored through the depth
- Fully oxidized regions have considerably higher ratio
- Oxidation layer size can be quantitatively measured.

Performance of Various Coating Materials



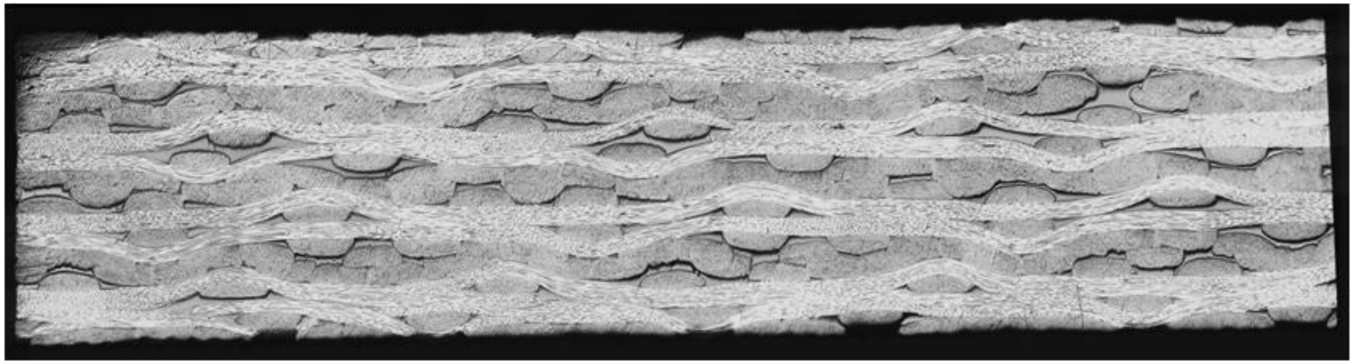
- Effectiveness correlates to the durability of the interface.
- Surface roughness did not provide additional mechanical bond strength or durability
- Between reactive metals - Cr bond layer is relatively more effective than Al.

Surface Damage Observations in T650-35/MVK-14 8HSW Textile Composites

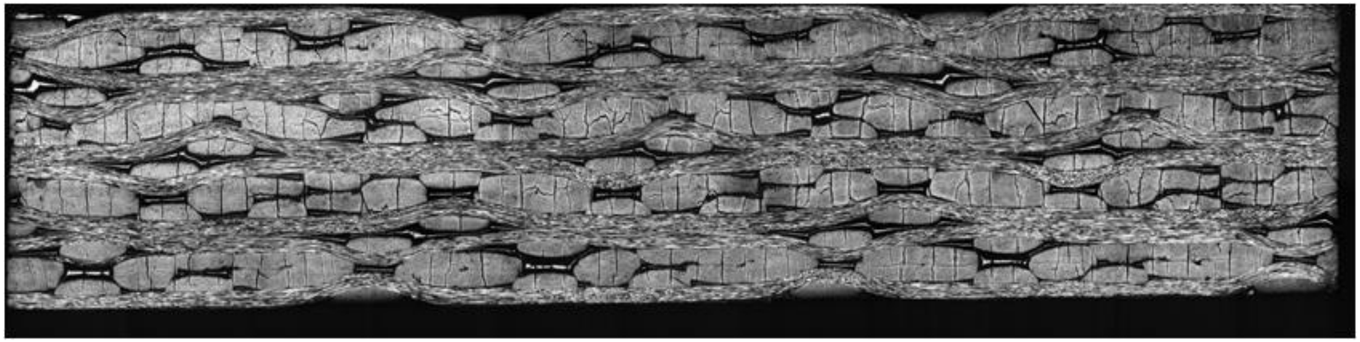


1250 hr

Lab Air, 15 Psi



Argon



Lab Air, 75 psi

Little damage in argon, while increase in surface crack density under elevated pressure

Concluding Remarks

- Coupling effects *for Oxidation-on-Damage evolution* (though material response changes) and *Damage-on-Oxidation* (creation of new surfaces) have been captured.
- What's next?
  - **Life prediction requires "careful" acceleration of "degradation"**
    - **Reduce scale of the specimens?**
    - **Not much room for temperature acceleration, pressure acceleration?**
    - **Analyze, characterize and control slow chemical degradation process?**
    - **New and novel structure visualization techniques, preferably non-destructive**

Questions?

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